

Chapter 3B: Mercury and Sulfur Environmental Assessment for the Everglades

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SUMMARY

This chapter updates the status of mercury and sulfur monitoring in the Everglades region and highlights progress on related research findings. All data presented in this chapter are reported for the calendar year unless otherwise noted. This chapter along with Volume III, Appendices 3-1 and 3-2, fulfills the Everglades Forever Act requirement that the South Florida Water Management District (SFWMD or District) and Florida Department of Environmental Protection (FDEP) annually issue a peer-reviewed report that summarizes all data and findings of mercury monitoring and research in the Everglades. Additional scientific information is available in the mercury-related chapters of the 1999 Everglades Interim Report, 2000–2004 Everglades Consolidated Reports, and 2005–2012 South Florida Environmental Reports – Volume I (www.sfwmd.gov/sfer).

WHY MERCURY IS A CONCERN

Mercury exposure causes human health effects including neurodevelopmental delays in children. Exposure to mercury as methylmercury (MeHg) is particularly hazardous for pregnant and breastfeeding women, as well as young children, since MeHg is most harmful in the early stages of development. Exposure to MeHg occurs primarily from consumption of fish containing MeHg; inorganic mercury is converted to MeHg by naturally occurring sulfate-reducing bacteria in water bodies and then concentrated up the aquatic food chain. MeHg also poses a threat to fish-eating wildlife species and species that prey on them (e.g. egrets, ibis, ospreys, eagles, otters, and panthers), potentially causing reproductive, neurological, and immune system problems.

The Everglades is particularly prone to high MeHg levels in fish due in part to the state's latitude, meteorology, and atmospheric chemistry which allow a high rate of mercury deposition from the atmosphere, as well as the Everglades biogeochemistry, which promotes efficient conversion of inorganic mercury from atmospheric deposition to the more toxic and bioaccumulative mercury form, MeHg.

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KEY FINDINGS OF RESEARCH AND MONITORING

Mercury in Everglades Fish and Wildlife

Based on monitoring in the Everglades Protection Area (EPA), methylmercury (methylmercury, or MeHg) levels in a great majority of game fish targeted by anglers, and fish consumed by wading birds and other wildlife, do not meet U.S. Environmental Protection Agency (USEPA, 1997; USEPA, 2001) guidance targets for protection of human health or wildlife.

Significant reductions in mercury (Hg) levels in fish in the WCAs in the early to mid-1990s were attributed to effective near-field (South Florida) reductions in atmospheric emissions (Axelrad et al., 2005). Subsequent to the reductions in mercury in fish observed until about year 2000, the median total mercury⁴ (THg) levels in largemouth bass (LMB) (*Micropterus salmoides*) in the WCAs have remained relatively unchanged (range of yearly medians, 0.30-0.55 mg/kg), and are generally above the USEPA MeHg guidance target for protection of human health (0.3 mg/kg), and for protection of fish-eating wildlife (0.346 mg/kg for trophic level 4 fish). In contrast, the median THg levels for LMB in Everglades National Park (ENP or Park) did not decline over the period 1989-2011 and continue to be higher and more variable than in the WCAs, with values ranging from 0.78-3.39 mg/kg.

For the period 2000–2011, 75 percent of trophic level 3 (TL3) sunfish sampled in the EPA exceeded the USEPA trophic level 3 MeHg wildlife protection guidance target of 0.077 mg/kg. The elevated concentrations of MeHg in fish correlated with elevated concentrations in wildlife. THg concentrations in panther hair⁴ (which is representative of body burdens) ranged from 0.092–67 mg/kg. THg has also been measured in great egret nestling feathers⁴ regularly since 1994 across the central EPA. Similar to the fish data, there has been no distinct trend since 2000 following initial declines in the 1990s.

In 2011, wood stork chicks (*Mycteria americana*, a state and federally listed endangered species) were sampled within the ENP from three coastal colonies and an inland colony. Coastal ENP colonies showed particularly high levels of feather THg, with means ranging from 5.2–10.8 mg/kg.

Mercury Sources to the Everglades

The Florida Department of Environmental Protection has developed a draft statewide Total Maximum Daily Load (TMDL) for mercury, which determined that a reduction in mercury of 86 percent from all nonpoint (atmospheric) anthropogenic mercury sources (from Florida, other U.S. states, and other countries), is necessary to protect public health. Mercury inputs to the EPA are overwhelmingly (greater than 95 percent) from atmospheric deposition, and originate predominantly (greater 95 percent) from sources outside of the U.S.

Mercury, Sulfur and Dissolved Organic Matter Biogeochemistry

There are both theoretical and empirical links between sulfate, dissolved organic matter (DOM), and inorganic mercury methylation, and there is clear evidence that sulfate concentrations are enriched anthropogenically throughout much of the Everglades. Because reducing mercury deposition to the Everglades via source control requires international cooperation (potentially requiring decades), other options that could achieve mercury reductions in fish tissue should be considered. Potential options for evaluation include regional reduction in sulfate inputs and managing the concentration and character of DOM. However, the role of sulfate and DOM in the biogeochemical cycling of mercury within the Everglades is complex and confounded by other variables, and these complexities must be understood and quantified before an effective strategy

to reduce MeHg levels through the control/management of sulfate and/or DOM can be designed and implemented.

Although there is evidence that sulfur concentrations in the Everglades have increased due to anthropogenic inputs, there is a need to better quantify all sources of sulfur to the system. Sulfate inputs to the EPA include three primary external sources: (1) inputs from atmospheric deposition, (2) inputs of connate seawater into canals, predominantly from those draining the Everglades Agricultural Area (EAA), and (3) the export of sulfate from the EAA, including sulfur that was originally applied as a soil amendment, sulfate released from EAA soil oxidation, and sulfate in surface waters released from Lake Okeechobee for agricultural or urban water supply or environmental purposes in the EPA. Sulfate may also be released from EPA soils through dryout and oxidation. Further investigation is needed to identify the relative contributions of these sources and the feasibility of managing sulfate in a manner that would result in a reduction of mercury methylation in the EPA.

Everglades marshes support high rates of organic carbon production (predominantly from calcareous periphyton and vascular plants) via photosynthesis. However, anthropogenic inputs of total phosphorus (TP) have resulted in enhanced production of DOM, with DOM concentrations generally greatest in the northern EPA and lowest further south in the ENP. The quality of DOM also changes across the nutrient enrichment gradient, with the DOM characteristic of the northern Everglades being more effective at making inorganic mercury bioavailable for methylation. There is a need to better assess both the effects of DOM on mercury methylation and the sources of DOM to evaluate the potential role of DOM in the state's restoration efforts.

Research Needs

Sulfur Mass Balanced Studies: An accurate sulfur mass balance is critical to better understanding the sulfur cycling in South Florida and for identifying any opportunities to sufficiently reduce sulfate loading to the EPA, lower MeHg levels in Everglades fish, and decrease potential risk to recreational anglers and fish-eating wildlife.

Monitoring and Modeling: Further development of the Everglades Mercury Cycling Model would allow better evaluation of management options for reducing mercury levels. To assess reducing the impacts of possible intrusion of connate seawater, it is recommended that a coupled hydrologic and water chemistry model be developed. The Everglades Landscape Model may be adapted to include sulfur cycling. The District has conducted preliminary data analysis on a sulfate budget for Lake Okeechobee. The Lake Okeechobee Environmental Model has a module capable of simulating lake-wide changes in sulfate concentrations under various hydrological conditions, which would assist in testing management options.

Dissolved Organic Matter (DOM): Research is needed to better understand the importance of the composition and concentrations of DOM that lead to enhanced MeHg production.

Effects of Sulfate on Mercury Methylation: The effects of changing sulfate concentrations on mercury methylation - particularly at low ambient sulfate concentrations - would benefit from further evaluation. Because the mercury methylation rate of sulfate-reducing bacteria is increased in the presence of both sulfate and DOM, the interaction of sulfate and DOM loadings on mercury methylation rate would also benefit from more research.

Bioaccumulation of Methylmercury in the Food Chain: MeHg concentrations increase up the food chain and display large variations in Everglades fish that cannot be explained by MeHg concentrations in surface water. Further studies are needed to assess seasonal changes in MeHg concentrations in fish at different trophic levels and the relationships with periphyton MeHg concentration, dietary composition, and MeHg concentrations.

Everglades Bird Habitat Restoration: Coastal ENP wood storks first sampled in 2011 showed particularly high levels of feather mercury. Ongoing hydrological restoration of the coastal zone is expected to result in an increased prey base there, and consequently, the greatest increase in numbers of wading birds in the Everglades. Therefore, the occurrence of high MeHg exposure to wading birds in this coastal zone area should be considered as part of Everglades habitat restoration planning.

MERCURY IN EVERGLADES FISH AND WILDLIFE

MERCURY IN LARGEMOUTH BASS

Ted Lange³, Curtis D. Pollman², Donald M. Axelrad¹
and Barbara Donner¹

Mercury concentrations in largemouth bass (LMB) (*Micropterus salmoides*) from the Water Conservation Areas (WCAs) were first measured in 1988 in fish from three interior canal locations, and the median total mercury (THg) concentration was 1.75 milligrams per kilogram (mg/kg) (range: 1.2–3.4 mg/kg, n=12). In subsequent years, additional monitoring locations were selected for annual sampling, representing both marsh and canal habitats. As shown in **Figure 3B-1**, eight sites within the Everglades Protection Area (EPA), including six sites within the WCAs and two sites within Shark River Slough in Everglades National Park (ENP or Park) are currently sampled annually. Additionally, LMB and other sport fish are sampled from other locations across the Greater Everglades, including the EPA, for assessing spatial and temporal trends in mercury in fish and potential risk to human health and wildlife.

Axial muscle tissue (fillets) from individual LMB was analyzed for THg to provide a temporally and spatially integrated measure of methylmercury (MeHg) exposure to a long-lived Everglades apex predator (Axelrad et al., 2011). MeHg bioaccumulation by LMB is influenced by several factors, including variations in prey availability and fish growth and movement, but most importantly by ambient MeHg concentrations across the landscape (Gu et al., 2012). While THg fish concentrations were analyzed in this study, more than 95 percent of the Hg found in top-level predatory fish such as LMB is in the form of MeHg (Grieb et al., 1990; Bloom, 1992) and, as such, THg levels are considered to be a reasonable approximation of MeHg concentrations.

During 2011, 116 LMB were collected from eight sites in the WCAs, a marked reduction from the total of 286 LMB collected in 2010. Fewer samples were due in part to extended periods of low water in the WCAs during summer 2011. Low water levels restricted fish to deep-water refugia (i.e., canals and alligator holes) for extended periods of time, and this resulted in reduced numbers of fish, particularly large-bodied fish (LMB and sunfish) encountered while sampling WCA marsh sites. Within Shark River Slough in the Park, a total of 40 LMB were collected from two sites during 2011 as well as an additional 20 LMB during early 2012. To date, 4,158 LMB from 52 locations have been collected from the EPA and surrounding areas (**Figure 3B-1**).

Distinctly different trends in LMB THg concentrations are evident between the WCAs and ENP Shark River Slough (**Figure 3B-2**) over the sampling period. In 2011, the median THg concentration in LMB in the WCAs was 0.46 mg/kg (range: 0.05–1.70 mg/kg, n=116), which represents a 27 percent decrease from 2010 and 66 percent decrease from the 1989 system-wide median LMB THg of 1.34 mg/kg (range: 0.25–3.90 mg/kg, n=89). LMB THg concentrations declined sharply during the 1990s across the WCAs possibly due to reductions in south Florida atmospheric emissions from municipal waste combustors and medical waste incinerators (Axelrad et al., 2005), but, since 2000, median concentrations have changed little, varying

between 0.30 (2001) and 0.55 (2010) mg/kg; the 2011 LMB THg median is within this range. While the region-wide trends in the WCAs show a strong downward trend over time, variations in LMB MeHg bioaccumulation continue to persist across the WCAs as a result of site-specific factors that influence Hg methylation rates (Gu et al., 2012). Current fish consumption advisories from the Florida Department of Health for the WCAs recommend that anglers limit and, in some cases, refrain from consuming LMB (FDOH, 2012).

In Shark River Slough, THg concentrations in LMB were monitored at two locations: (1) L-67 Extension Canal (L67F1) where waters enter the ENP from WCA-3, and (2) North Prong Creek (ENPNP), located in ecotonal habitat situated between the sawgrass marsh of Shark River Slough and mangrove estuary of the Shark River (**Figure 3B-1**). In 2011, 40 LMB from Shark River Slough had a median THg concentration of 1.3 mg/kg (range: 0.30–2.35 mg/kg, n=40) representing a decline of 16 percent from 2010 and an increase of 26 percent from the median concentration measured in 1994, the first year LMB were collected from site ENPNP at the south end of Shark River Slough (**Figure 3B-2**). For 2012, THg in LMB from ENP Shark River Slough (median THg = 0.98 mg/kg; n = 20) includes data from only one site (ENPNP), as this year's sampling has not been completed.

Between 1989 and 2011, the median annual THg concentration in Shark River Slough LMB ranged between 0.78 and 3.39 mg/kg (**Figure 3B-2**), but there were no clear trends over the sampling period. However, it is clearly recognizable that all LMB collected from the slough area from 1989–2012 (n = 609), with the exception of one fish collected in 1998, have exceeded the 0.3 mg/kg U.S. Environmental Protection Agency (USEPA, 2001) recommended MeHg criterion for the protection of human health, and the annual median THg exceeded 1 mg/kg in 16 of 20 sampling years (i.e., except in 1993, 1998, 1999, and 2008). This has resulted in warnings to anglers to avoid consuming LMB from the freshwater reaches of Shark River Slough (FDOH, 2012).

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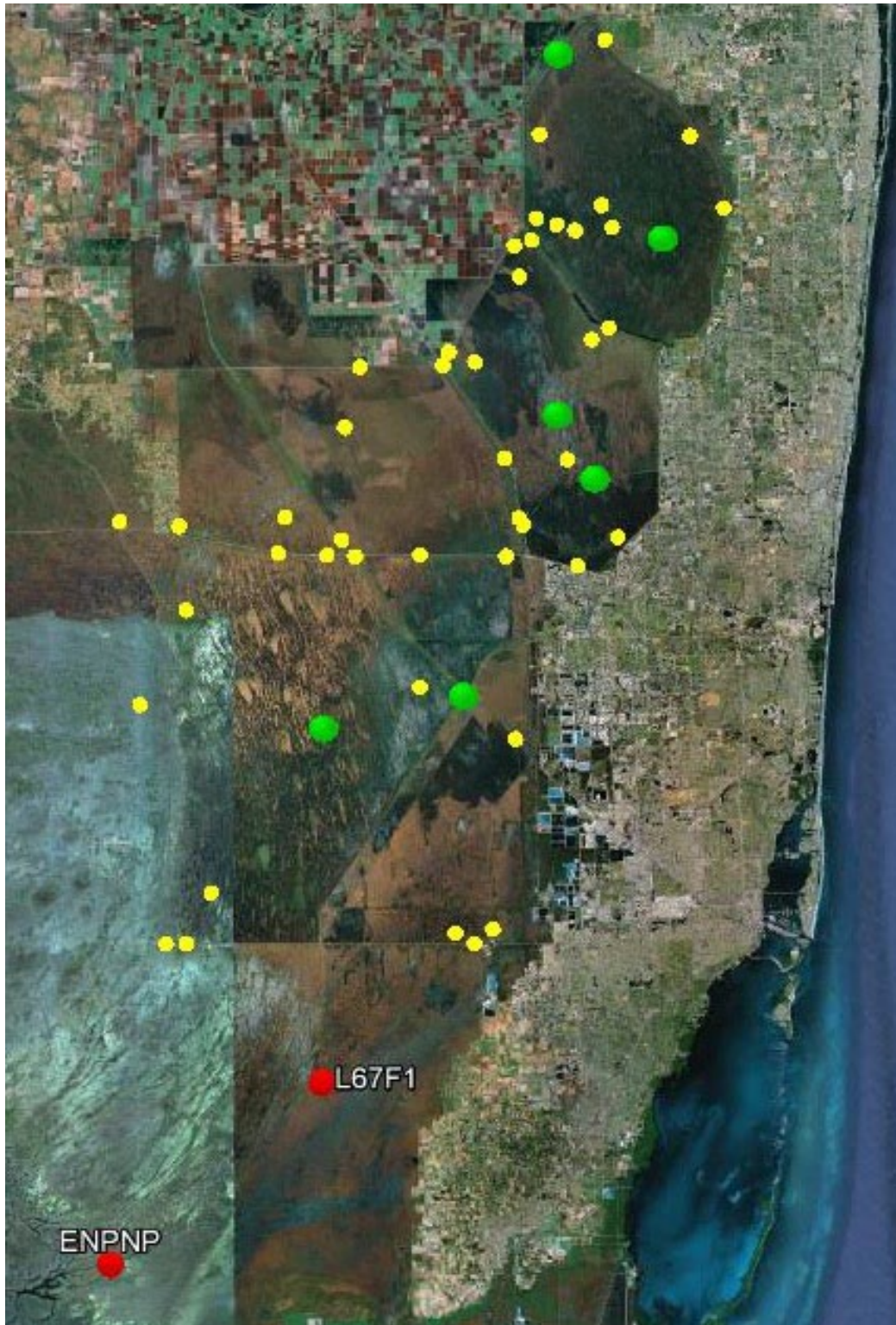


Figure 3B-1. Largemouth bass (LMB; *Micropterus salmoides*) sampling locations in the Everglades Protection Area (EPA) from 1988–2012. Long-term monitoring sites are visited annually in the Water Conservation Areas (WCAs) (●) and Shark River Slough in Everglades National Park (ENP or Park) (●). All others (●) are located in the WCAs and visited periodically to assess trends and potential risk to human health and wildlife from consuming fish.

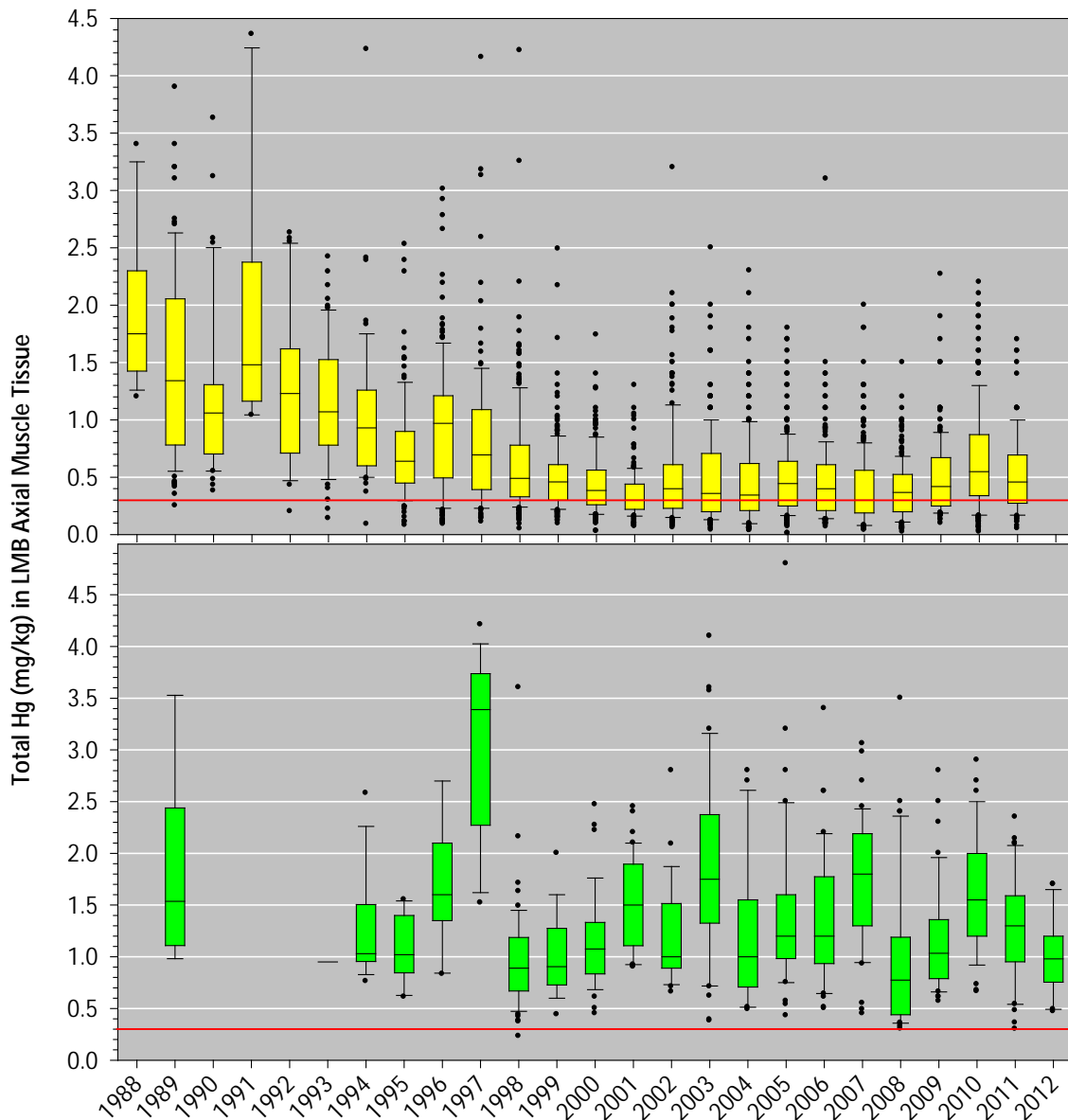


Figure 3B-2. Annual summaries of total mercury (THg) in muscle tissue of 4,158 LMB collected from canal and marsh sites in the EPA from 1988–2012 from regional groupings within WCA-1, WCA-2, and WCA-3 (n=50 sites; 3,549 fish) (top) and (B) Shark River Slough in the Park (n=2 sites; 609 fish) (bottom). Box plots represent the median and 25th and 75th percentiles, whiskers represent the 10th and 90th percentiles, and points are outliers. The red line indicates the 0.3 mg/kg U.S. Environmental Protection Agency fish tissue methylmercury (MeHg) criterion for protection of human health (USEPA, 2001). The USEPA fish tissue MeHg criterion for protection of wildlife for trophic level (TL) 4 fish is 0.346 mg/kg (USEPA, 1997).

MERCURY IN EVERGLADES LARGEMOUTH BASS VERSUS STATEWIDE LEVELS

Ted Lange³ and Curtis D. Pollman²

A total of 703 largemouth bass were collected from the Greater Everglades and analyzed for muscle tissue THg concentrations in 2010 and 2011. Sampling included 38 different locations in 2010 (439 fish collected) and 22 different locations in 2011 (264 fish collected), with 17 sites sampled during both years, and 26 sites sampled during only one of the two years. In aggregate, 40 unique stations were sampled by the Florida Fish and Wildlife Conservation Commission (FWC), including two sites near the northeast shore of Lake Okeechobee, 11 sites associated with the Everglades Stormwater Treatment Areas (STAs), two sites within the Everglades Agricultural Area (EAA)—Holeyland and Rotenberger Wildlife Management Areas (WMAs), three sites west of the EPA, and two sites immediately to the north and east of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge). The remaining 20 sites are located within the marsh or in canals of the EPA.

LMB THg concentrations were normalized to a 15-inch length to facilitate comparison with LMB concentration data developed for Florida lakes and streams as part of the FDEP statewide Hg Total Maximum Daily Load (TMDL) analysis (also normalized to 15-inch length).⁴ In both the statewide Hg TMDL study and in this analysis, normalization was conducted using robust regression (StataCorp, 2012) to minimize the influence of outliers on the fitted model parameter estimates. Robust regression was conducted using site location and sample year as categorical variables to develop site-specific slopes for all sites with a minimum of five observations. This latter constraint was imposed to ensure stable output and resulted in excluding data from nine sites ($n = 23$).

The normalized Hg concentrations, Hg_{LMB15} , were initially compared across sites sampled in both 2010 and 2011 to assess whether there was a consistent difference in results between the two years. This analysis was conducted using a paired t-test for 14 sites (three of the sites sampled in both years lacked sufficient specimens for at least one of the two years). The comparison showed no consistent difference in paired observations across the two years ($p = 0.2512$, two-tailed test) and, as a result, the data from 2010 and 2011 were combined across sites to estimate the cumulative frequency distribution for Hg_{LMB15} .

The distribution of Hg_{LMB15} for Everglades sites were compared with the distribution for the same metric for Florida lakes ($n = 130$) and streams ($n = 128$) sampled between September 2008 and September 2010 as part of the statewide Hg TMDL conducted by the FDEP (2012a). In this

⁴ The set of lakes and rivers/streams selected for sampling for the statewide mercury Total Maximum Daily Load (Hg TMDL) (FDEP, 2012a) was developed using data collected randomly from a matrix of water bodies segregated by key physical and chemical water body characteristics, with the goal of obtaining an even distribution of study sites spanning a wide range of the target variables. Preliminary analyses identified a set of three target variables (pH, color, and chlorophyll *a* for lakes; pH, color, and nitrate for streams) that were important determinants of the variability of fish tissue Hg concentrations; the selection of lake and stream sites for sampling in turn was based on the joint distribution of these three target variables across five concentration intervals for each variable. This yielded a possible 125 unique variable interval combinations (5x5x5) or sampling bins. Additional lakes and streams were sampled randomly from individual bins to produce a total number of lake and stream reaches or segments of 130 lakes and 128 streams for each water body type. Prospective lakes and streams were selected from FDEP Status Monitoring Network database (Pollman, 2012a).

analysis, both sites located within the EAA and other sites associated with the STAs were excluded because these sites are not considered to be representative of the canals and marshes of the EPA. In addition, eight TMDL stream sites located within or near the EPA were included with the FWC dataset to conduct the distributional analysis. The results from the distributional analysis are shown in **Figure 3B-3** as both box plots and cumulative frequency curves. These results, which are unweighted for area, indicate that the distribution of fish tissue Hg concentrations in the Everglades is higher compared to that observed in Florida streams and rivers external to the Everglades and substantially higher than concentrations found in Florida lakes. For example, the median Hg_{LMB15} for Everglades sites was 0.689 mg/kg, compared to 0.38 mg/kg and 0.603 mg/kg for the Hg TMDL lakes and streams (excluding Everglades sites), respectively. Differences in mean values for Everglades LMB compared to mean concentrations observed in Florida lakes and streams were evaluated non-parametrically using the Wilcoxon/Kruskal-Wallis test (SAS, 2011). Although the distribution of LMB Hg concentrations in Everglades samples were normal (Shapiro-Wilks test; $p = 0.0626$), the distribution of LMB Hg concentrations in both streams and lake were not, nor did log transforming the data acceptably resolve the non-normality problem. Results from the Wilcoxon test, which was implemented for each possible paired comparison, indicate that mean concentrations of LMB Hg in the Everglades (0.769 mg/kg) are significantly higher than concentrations observed in lakes (mean equals 0.450 mg/kg, $p < 0.001$); but statistically indistinguishable from streams (mean equals 0.644 mg/kg, $p = 0.1660$).

Figure 3B-4 shows the spatial distribution of Hg_{LMB15} values for the 32 South Florida sites included in the distribution analysis. Within the EPA, the highest concentrations were observed in the ENP, followed by sites located in the north central interior of WCA-3A. Lower concentrations were observed for sites in the northern EPA associated with canal waters exiting the EAA or interior stations where the water chemistry is heavily influenced by waters exiting the EAA.

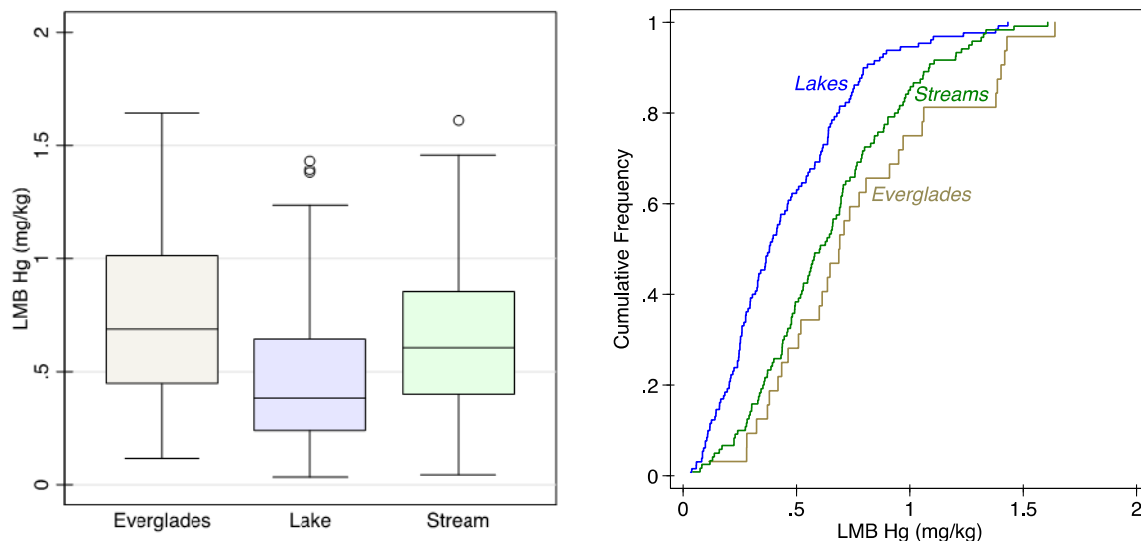


Figure 3B-3. Box plot (left) and cumulative frequency distribution plot (right) comparing standardized LMB (15") THg concentrations measured in the Everglades (averaged across 2010 and 2011 for those sites sampled during both years) with standardized LMB Hg concentrations measured in the Florida Department of Environmental Protection (FDEP) statewide Hg Total Maximum Daily Load (TMDL) study from 2008–2010. Box plots represent median and 25th, and 75th percentiles; whiskers represent 10th and 90th percentiles; and points are outliers. Sample numbers are as follows: Everglades (including 8 Hg TMDL stream sites located within the EPA = 32), and Florida lakes = 130 and streams = 120 (external to the EPA).

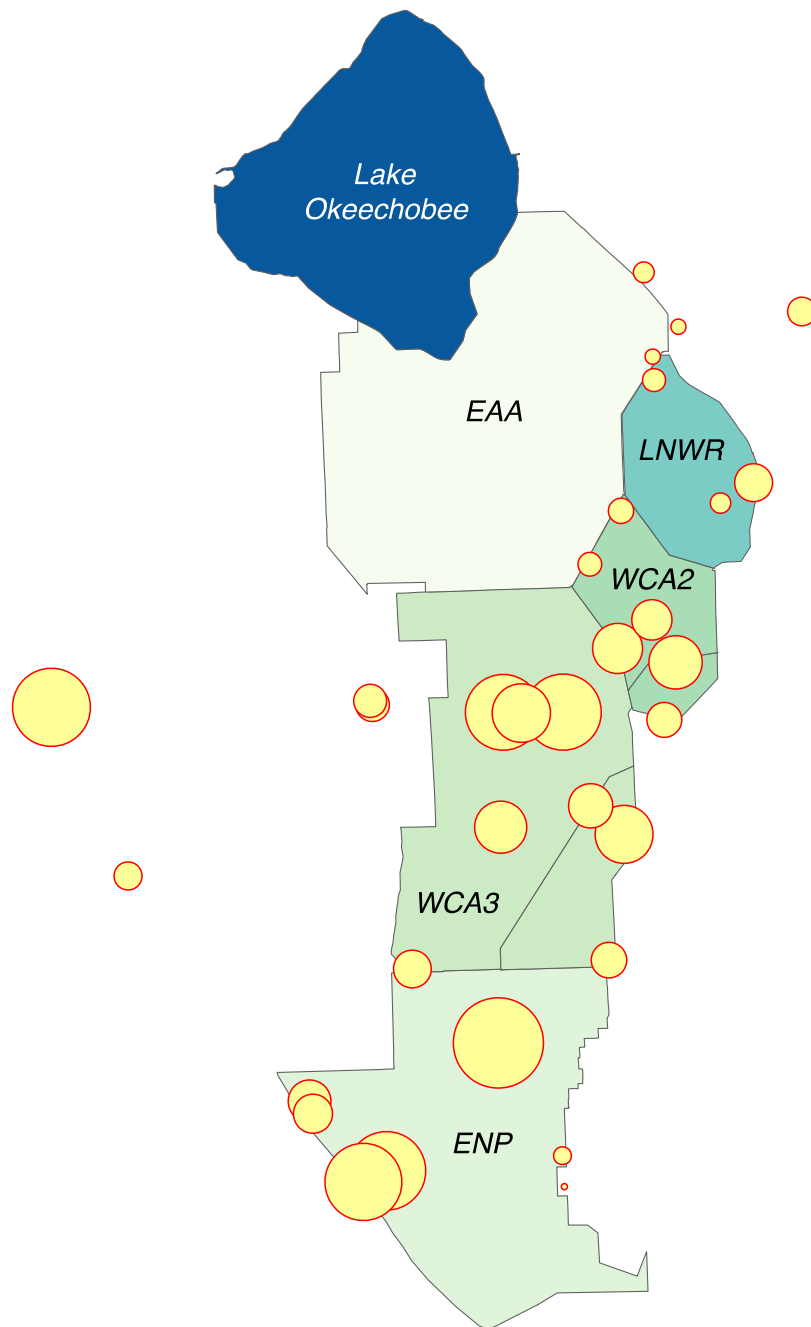


Figure 3B-4. LMB Hg concentrations normalized to 15" length. Circle size is proportional to the squared value of the normalized concentration. Squaring the values of Hg_{LMB15} was conducted to facilitate visualizing differences in concentration between sites. Data plotted include 8 Everglades stream sites sampled as part of the Florida statewide Hg TMDL, plus 24 sites sampled in 2010 and 2011 by the Florida Fish and Wildlife Conservation Commission. Range of Hg_{LMB15} is 0.113 to 1.64 milligrams per kilogram (mg/kg).

MERCURY IN MOSQUITOFISH AND SUNFISH

Ben Gu, Ted Lange³ and Donald M. Axelrad¹

Mosquitofish

Mosquitofish (*Gambusia* spp.) have been analyzed for THg from across the EPA and Holey Land and Rotenberger WMAs since 1998 (**Figure 3B-5**). During 2011, whole-body concentrations of THg concentrations in mosquitofish from 12 monitoring sites ranged from 21 nanograms per gram (ng/g = 10^{-3} mg/kg) at WCA2F1 to 373 ng/g at WCA2U3, and levels were higher in 2011 than in 2010 at most sites. However, there was no significant temporal trend in THg in mosquitofish over the period of record (POR) for any of the sites (Spearman Rank Order Correlation, all $p > 0.05$).

In 2011, median THg concentrations in mosquitofish exceeded the federal criterion of 77 ng/g MeHg for trophic level (TL) 3 fish for protection of wildlife (USEPA, 1997) at nine of the 12 monitoring sites⁵. As noted previously in the *Mercury in Largemouth Bass* section, it is generally accepted that greater than 95 percent of mercury found in high trophic level fish is in the form of MeHg. This is supported by recent LMB and sunfish surveys by the District in the Everglades study area (88–100 percent MeHg; $n = 9$). However for lower trophic level fish such as mosquitofish, current Everglades surveys using composite fish samples collected from the STAs (mean MeHg \times 100/mean THg = 54%; $n = 5$) and an earlier survey of WCA-2A fish (mean MeHg \times 100/mean THg = 73%; $n = 25$) by the District indicate that MeHg as a proportion of THg spans a much wider range (i.e., 13–100%).

The highest basin-wide THg in mosquitofish concentration (201 ng/g) was found in 1999 and the lowest (28 ng/g) in 2005. Low THg concentrations (i.e., less than 77 ng/g) in mosquitofish were found in wet years (1999, 2001–2006, and 2010), and THg levels greater than 77 ng/g were typically associated with drought years. Drought conditions have been found to promote sulfate (SO_4^{2-}) and Hg oxidation and consequently high rates of mercury methylation in the Everglades (Gilmour et al., 2004; Rumbold and Fink, 2006). The annual median THg levels in mosquitofish in WCA-1 (58 ng/g) and WCA-2 (52 ng/g) were less than WCA-3 (75 ng/g) and L67F1 (73 ng/g) in the ENP Shark River Slough, but these differences are not statistically significant (Kruskal-Wallis Analysis, $p = 0.204$). Mosquitofish THg concentrations in 2011 from Holey Land (50 ng/g) and Rotenberger (45 ng/g) were similar although the annual median value (80 ng/g) in Rotenberger was nearly twice that of Holey Land (42 ng/g) for the POR.

Sunfish

Four sunfish species [bluegill (*Lepomis macrochirus*), redeared sunfish (*L. microlophus*), spotted sunfish (*L. punctatus*) and warmouth (*L. gulosus*)] have been sampled for THg analysis from across the EPA and Holey Land and Rotenberger WMAs since 1998 (**Figure 3B-6**).

⁵ Note that TL3 criterion is used as a surrogate for mosquitofish (*Gambusia* spp.) which is considered to be representative of fish species between TL2 and TL3. MeHg to THg ratio in *Gambusia* is lower than that of sunfish or LMB, but its variability and limited data preclude adjustment of *Gambusia* THg to MeHg values. Based on available data, the rates of mercury methylation and dietary composition of *Gambusia* change seasonally in response to hydrology and food availability and, therefore, the ratio of MeHg/THg in this species also depends on sampling season and locations; further study is needed to better understand the seasonal changes in MeHg levels in *Gambusia*.

189±173 ng/g (n = 3018), with the median value lowest in redeared sunfish (118 ng/g), followed by bluegill (193 ng/g) and warmouth (249 ng/g), and highest in spotted sunfish (258 ng/g). The median THg level for the POR was highest (390 ng/g for all sunfish and 416 ng/g for bluegill) at the ENP (L67F1). Average THg concentrations for all sunfish and bluegill at CA315 and WCA2U3 were also above 200 ng/g. During 2011, THg concentrations in the sunfish assemblage from 12 monitoring sites ranged from 59 ng/g at WCA2F1 to 371 ng/g at L67F1 (ENP). Except for two sites, THg levels exceeded the federal MeHg criterion of 77 ng/g for TL3 fish for protection of wildlife. Bluegill is the most common of the four sampled sunfish in the EPA, with median THg concentrations ranging from 59 ng/g (WCA2F1) to 394 ng/g (L67F1) during 2011.

THg concentrations for the POR varied among sunfish species at each site (**Figure 3B-7**), with no consistent trends among sites or years. For the ENP, bluegill and warmouth displayed THg values higher than those for redeared and spotted sunfish. These two species also displayed higher values than other sunfish species in WCA-1 and Rotenberger WMA. There is a clear north to south trend of increasing THg concentrations in bluegill, redeared sunfish, and warmouth in the EPA. Trend analysis (Spearman Rank Order Correlation) on all sunfish species collected indicates significant increases at Holey Land ($r = 0.537$, $p = 0.044$, $n = 14$ years) and Rotenberger ($r = 0.69$, $p = 0.047$, $n = 8$ years) over time, while no significant trend was detected from other sites. THg concentration in bluegill displayed a significant uptrend in WCA-2 ($r = 0.71$, $p = 0.005$, $n = 14$ years) (**Figure 3B-7**).

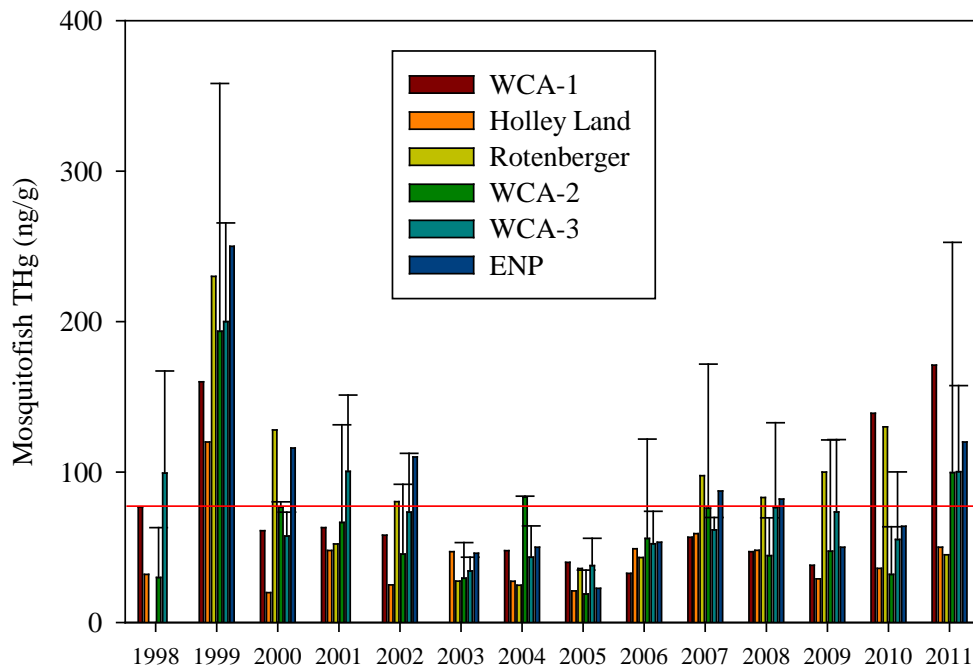


Figure 3B-5. Annual THg concentrations in mosquitofish (*Gambusia* spp.) at each monitoring site from 1998–2011. Error bars represent one standard deviation of multiple sites within each main water body. Red line is 77 ng/g USEPA MeHg criterion for TL3 fish for protection of wildlife.⁵

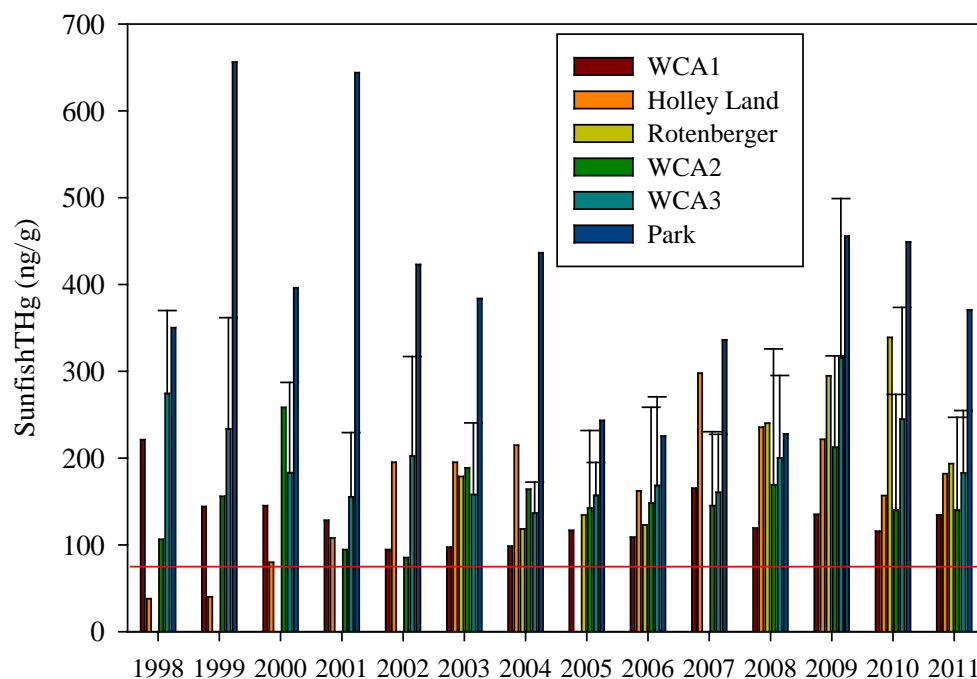


Figure 3B-6. Annual THg concentrations in sunfish at each monitoring site from 1998–2011. Error bars represent one standard deviation of multiple sites within each main water body. Red line is 77 ng/g USEPA MeHg criterion for TL3 fish for protection of wildlife.

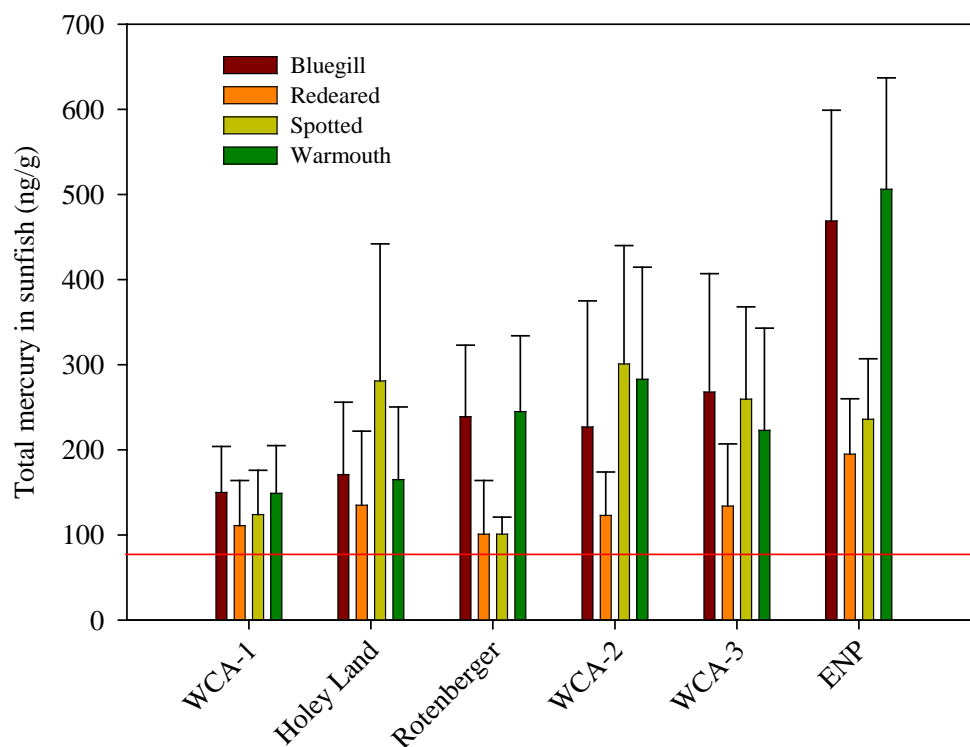


Figure 3B-7. THg concentrations in individual sunfish species at WCA-1 (LOXF4), WCA-2 (U3), WCA-3 (CA315), and ENP (L67F1) from 1998–2011. Error bars represent one standard deviation of multiple sites within each main water body. Red line is 77 ng/g USEPA MeHg criterion for TL3 fish for protection of wildlife.

MERCURY IN PANTHERS

Mark W. Cunningham⁶

The Florida panther (*Puma concolor coryi*) is a federally and state-listed endangered subspecies, and stressors including environmental contaminants (Roelke et al., 1991; Facemire et al., 1995), infectious diseases (Cunningham et al., 2008), low genetic variability (Johnson et al., 2010), and habitat loss have contributed to the decline of this species. To monitor mercury burdens in the panther population, 136 hair samples from 124 free-ranging Florida panthers sampled in South Florida from 2008–2012 were collected at capture or necropsy and analyzed for THg by the FDEP. Areas sampled included public and private lands north of I-75 [including the Florida Panther National Wildlife Refuge and Bear Island and Addition Land Units of Big Cypress National Preserve (BCNP)], Fakahatchee Strand State Preserve, Picayune Strand State Forest, and BCNP south of I-75. The ENP and eastern Everglades were not sampled during this time period. THg concentrations in panther hair ranged from 0.092 to 67 parts per million (ppm).

While detailed analyses are pending, preliminary observations indicate that seven of the 10 panthers with the highest THg concentrations (ranging from 20 to 67 parts per million, or ppm) were sampled from the BCNP south of I-75. Only one panther north of I-75 (BCNP) was in the top ten, with THg hair concentrations of 20 ppm. This supports Brandon's (2011) observation of increasing THg concentrations in the BCNP (north and south of I-75 combined) between 1978 and 2007. The cause of this apparent increase in panther THg in the BCNP is unknown but may be due to shifts in prey availability. Observed declines in white-tailed deer and feral hog numbers in some portions of the BCNP may have caused a greater dependence by panthers on prey species with higher THg burdens such as raccoons and alligators (Brandon, 2011).

MERCURY IN GREAT EGRETS AND WOOD STORKS

Peter Frederick⁷

Mercury Levels in Great Egrets

Mercury has been sampled in great egret (*Ardea alba*) nestlings regularly since 1994 over much of the central EPA (Figure 3B-8). Mercury is determined for feathers, which are excellent accumulators and integrators of mercury body burden (Burger, 1993; Furness et al., 1986). Feathers are sampled from great egrets, which are a good representative high trophic level predator, feeding almost exclusively on small to medium sized fishes (McCrimmon et al., 2011). Feathers are from large nestlings (28 to 35 days), which have all of their food harvested from approximately a 25 km radius of the nesting colony; this ensures that the mercury signal is local (McCrimmon et al., 2011). Eight to 15 young are sampled from each colony each year, all from different nests. Although mercury was measured as THg, nearly all the mercury in feather tissue is in the methylated form (Frederick et al., 2004).

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The broad trend in the data is that mercury levels in great egrets fell sharply from a high in 1997 (mean across colonies = 20.68 ppm fresh weight) to a low in 2003 (mean = 2.15 ppm fresh weight) (**Figure 3B-9**). Since 2003, mercury levels have risen somewhat consistently by year, to a mean of 7.79 ppm in 2011. While the trend is robust, it is important to understand that there appears to be relatively high variance in measurements at colonies from year to year, and the colonies sampled have also changed over time, partly due to logistics of sampling and partly because some colonies are no longer active (**Figure 3B-10**). This results in some uncertainty about the absolute magnitude of change over the years (see standard deviations in **Figure 3B-9**).

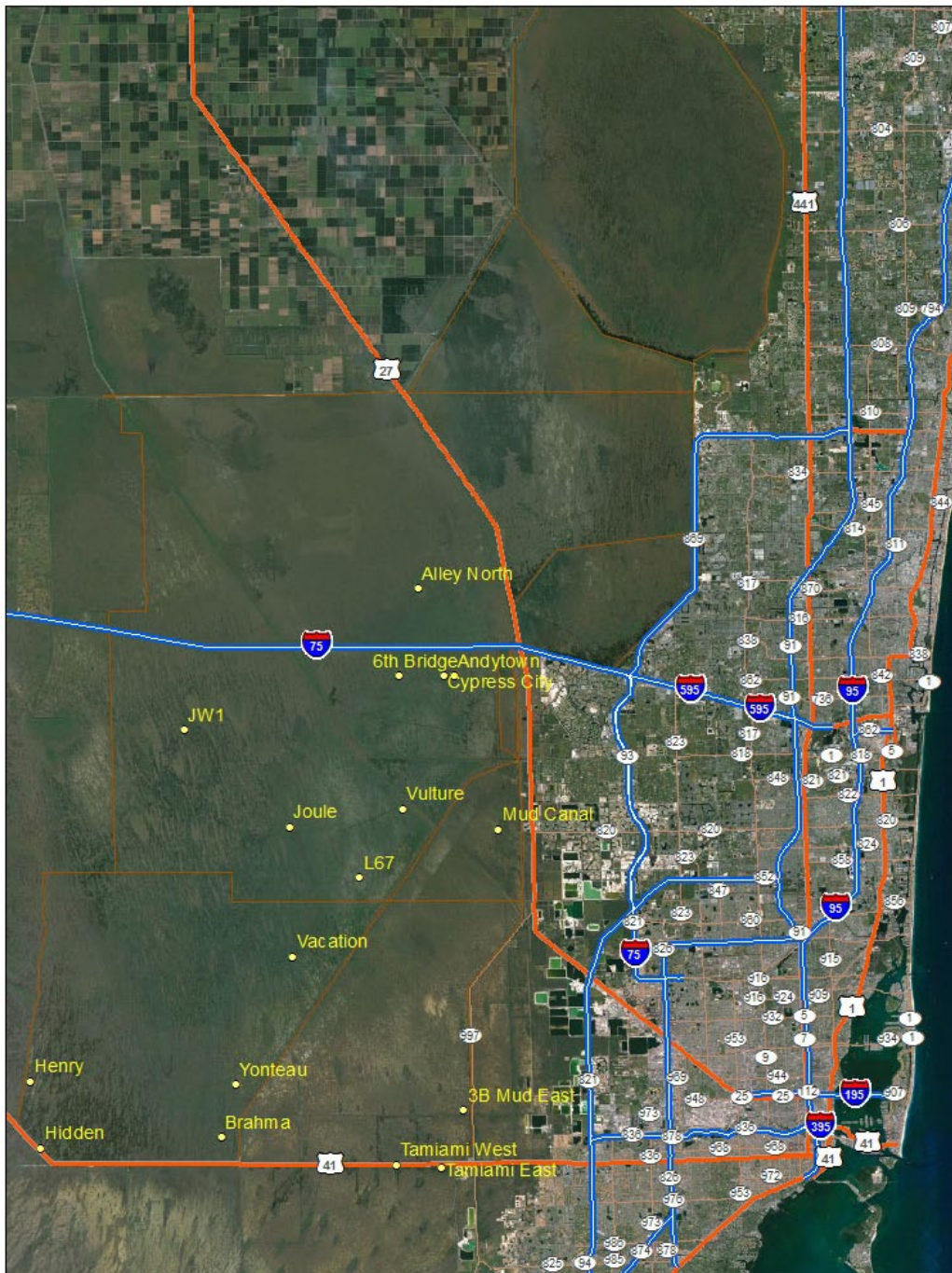


Figure 3B-8. Everglades great egret (*Ardea alba*) colony locations where feathers from nestlings were sampled from 1994–2011.

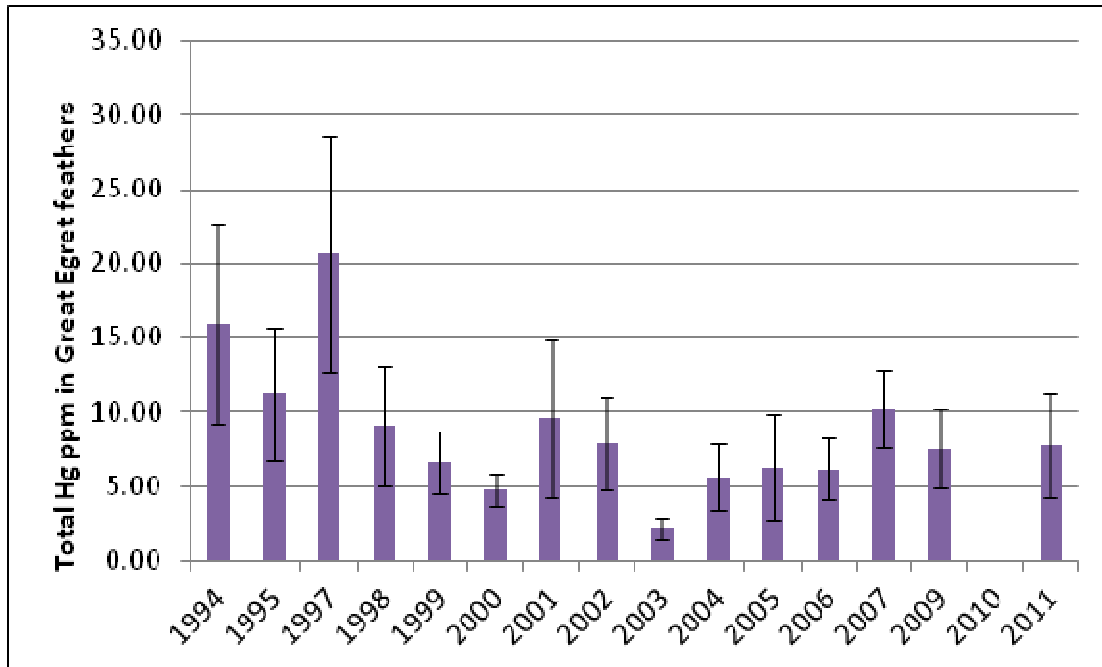


Figure 3B-9. Mean (± 1 SD) THg in feather tissue of great egret nestlings in the central EPA (1994–2011). Means are of colonies spaced across the EPA.

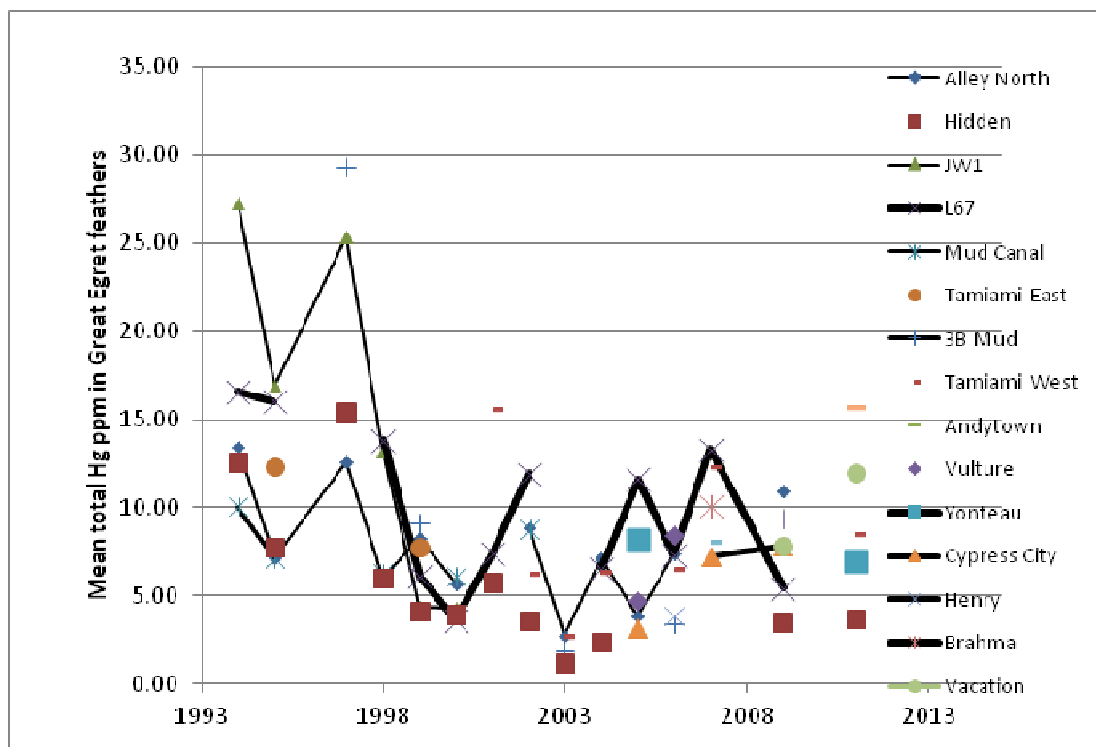


Figure 3B-10. Mean annual THg in feather tissue of great egret nestlings by colony in the central EPA (1994–2011). Different symbols represent different colonies; lines represent continuous data from individual colonies for three or more continuous years.

Coastal Versus Inland Mercury Levels in Wood Storks

Feathers from wood stork (*Mycteria americana*) chicks have been sampled from inland colonies from 2002–2005 using the same methods as previously noted for great egrets. However, colonies in the coastal parts of the Everglades have not been sampled, despite increasing numbers of wading birds nesting in that area. In 2011, a cooperative project was initiated with the ENP, and wood stork chicks were sampled in coastal colonies (Paurotis Pond, Cuthbert Lake, and Broad River) as well as at the inland Tamiami West colony. As depicted in **Figure 3B-11**, data suggest that THg contamination in the Tamiami West colony has fluctuated considerably over time, ranging from approximately 2 to 8 ppm, even in adjacent years (e.g., 2003 versus 2002, respectively). Coastal ENP colonies in 2011 showed particularly high levels of feather mercury, with means of 10.8 ppm (Cuthbert Lake), 8.4 ppm (Paurotis Pond), and 5.2 ppm (Broad River). These relatively high levels are of particular concern because with hydrological restoration the coastal zone area is expected to have the most dramatic restoration of prey base, and consequent greatest increase in numbers of wading birds in the system. In part because the coastal zone area was historically the area that hosted the greatest nesting numbers, one of the restoration goals for wading birds is to increase the proportion of the population that nests in the estuarine zone. Therefore, the occurrence of high MeHg exposure to wading birds in this coastal zone area should be consideration regarding Everglades habitat restoration.

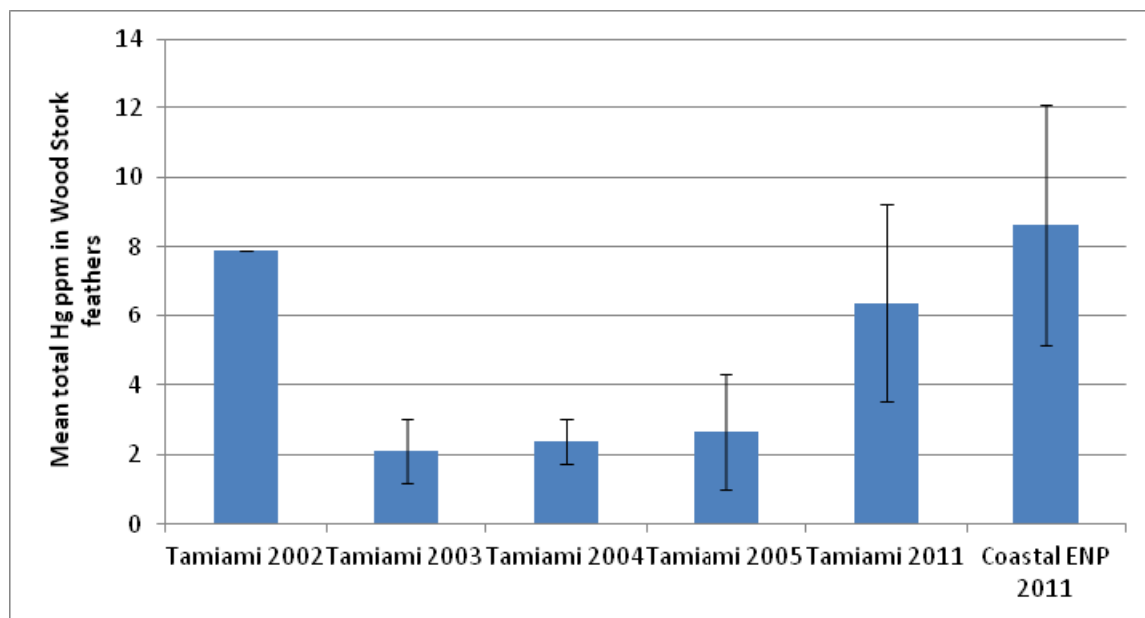


Figure 3B-11. Mean THg in wood stork (*Mycteria americana*) nestling feathers (± 1 SD) at the freshwater Tamiami West colony and at coastal locations. Note that coastal locations have been sampled for the first time in 2011. "Coastal ENP" is an average of all samples collected at Paurotis Pond, Cuthbert Lake, and Broad River colonies.

WADING BIRDS TRANSPORT MERCURY FROM MARSHES TO TREE ISLANDS

Ben Gu, Lena Ma⁸, Donny Smoak⁹, Sharon Ewe¹⁰, Yingjia Zhu⁸, Daniel Irick⁸, Michael Ross¹¹ and Yuncong Li⁸

The transport of persistent pollutants by seabirds from ocean to land has been documented in recent studies (Blais et al., 2005; Michelutti et al., 2010). Many seabirds are top predators in aquatic food chains, accumulating nutrients and pollutants through biomagnification. High mercury concentrations in fish and other wildlife species from the Everglades have been reported (Frederick et al., 2005). The Everglades makes up the largest peatland in the United States, consisting of 90 percent shallow marsh and 10 percent upland (tree islands). Wading birds are implicated in phosphorus enrichment in tree island soils (Wetzel et al., 2011). Notably in this study, for the first time wading birds are linked to mercury contamination in the Everglades tree island soil by guano accumulation. The transport of mercury from marsh to upland areas in the Everglades is widespread and has taken place for some time.

In this three-year study, surface soil samples were collected from 26 tree islands across the EPA along with three dated soil cores from two tree islands and samples from a marsh in the central EPA (**Figure 3B-12**, panel A). Wading birds such as the great egret, white ibis (*Eudocimus albus*), and wood stork are common predators in the Everglades that consume small fish or crustaceans from the marsh, and roost and breed on selected tree islands. The linkage between wading birds and tree islands was established by measuring THg and stable nitrogen isotopes ($\delta^{15}\text{N}$), both of which increased along food chains. Unlike marsh soil, upland vegetation, prey fish, and droppings from other wild animals, wading bird guano was enriched with both mercury and $\delta^{15}\text{N}$ (**Table 3B-1**).

Table 3B-1. THg concentration and stable nitrogen isotope values (mean \pm SD, n) in soil, biota, and guano samples from the EPA (2008–2010).

Sample type	THg (mg kg ⁻¹)	$\delta^{15}\text{N}$ (‰)
Marsh soil	0.16 \pm 0.14, 600 ^a	2.6 \pm 0.8, 5 ^b
Tree island plants ^b	0.05 \pm 0.03, 11	2.3 \pm 2.8, 20
Mammal droppings ^b	0.11 \pm 0.10, 8	3.2 \pm 2.6, 11
Wading bird guano ^c	0.22 \pm 0.06, 5	8.4 \pm 0.6, 12
Mosquitofish (<i>Gambusia affinis</i>)	0.08 \pm 0.05, 10 ^d	10.1 \pm 1.3, 10 ^b
Sunfish (<i>Lepomis</i> spp.)	0.16 \pm 0.08, 10 ^d	11.2 \pm 2.4, 10 ^b
Great egret (<i>Ardea alba</i>) feather	4.5 \pm 4.2, 305 ^d	9.1, 2

Data Sources: ^a Cohen et al., 2008; ^b this study; ^c Guano samples are a mix of wading bird species: great egret (*Ardea alba*), snowy egret (*Egretta thula*), white ibis (*Eudocimus albus*), little blue heron (*E. caerulea*), and tri-colored heron (*E. tricolor*); ^d District's DBHYDRO database (www.sfwmd.gov/dbhydro).

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THg concentrations and $\delta^{15}\text{N}$ values from the 26 tree island soil formed two distinct clusters (**Figure 3B-12**, panel B). Approximately 40 percent of the tree islands investigated had high THg concentrations (0.41 ± 0.13 mg/kg) and were enriched with $\delta^{15}\text{N}$ ($10.2 \pm 1.2\text{‰}$), compared to only 0.13 ± 0.04 mg/kg in THg and $3.9 \pm 1.7\text{‰}$ in $\delta^{15}\text{N}$ from 60 percent of the tree islands, which are similar to the background values in marsh soil (**Table 3B-1**). These data suggest that wading birds, instead of other wildlife, are biovectors for mercury transport from marshes to the residence tree islands. The proportion of tree islands influenced by wading birds is considerably higher than previously estimated (Wetzel et al., 2011). All tree islands sampled from the Shark River Slough in the ENP were mercury hotspots.

Dated soil cores collected from one unaffected, one affected tree island, and its nearby marsh displayed drastic differences in THg concentrations (**Figure 3B-12**, panel C) and $\delta^{15}\text{N}$ values (**Figure 3B-12**, panel D) over about the last 150 years. The average THg concentration (0.54 ± 0.15 mg kg⁻¹) and $\delta^{15}\text{N}$ value ($9.6 \pm 0.7\text{‰}$) in the affected island soil were fivefold and two trophic levels higher than the unaffected island (THg = 0.11 ± 0.04 mg kg⁻¹, $\delta^{15}\text{N}$ = $1.7 \pm 0.7\text{‰}$) and the marsh (THg = 0.11 ± 0.09 mg kg⁻¹, $\delta^{15}\text{N}$ = $3.7 \pm 0.5\text{‰}$). The trend of increasing mercury concentrations since the turn of the last century has been closely associated with the increase in atmospheric mercury deposition in South Florida (Rood et al., 1995), as well as enhanced mercury methylation (Gilmour et al., 1998) and accumulation in food webs resulting from high sulfate loading from the northern EPA (Frederick et al., 2005). A trend of decreasing mercury concentration in all cores after the 1990s (**Figure 3B-12**, panel C) corresponded well with the decreases in mercury bioaccumulation in fish and wading birds due to local reduction in mercury emissions (Frederick et al., 2005).

Avian transport of contaminants is common in coastal regions (Blais et al., 2005; Michelutti et al., 2010) and has recently been found in inland waters (Cristol et al., 2008) as well as the Everglades. Many wildlife species in the Everglades contain mercury concentrations exceeding federal criteria for animal health (Frederick et al., 2005). The deposition of Hg-laden guano acquired from food in the aquatic ecosystem by migrating birds has contaminated terrestrial soil and food webs (Cristol et al., 2008). On the other hand, considering that 95 percent of mercury in top-level prey fish consists of MeHg and 90 percent of the tree islands have lost its woody vegetation due to major hydrological modifications in the Everglades, dispersal of both new and historical mercury to marshes during the wet season and by soil erosion from the degraded tree islands may contribute to some of the localized hotspots in the Everglades, although this hypothesis warrants further research.

453

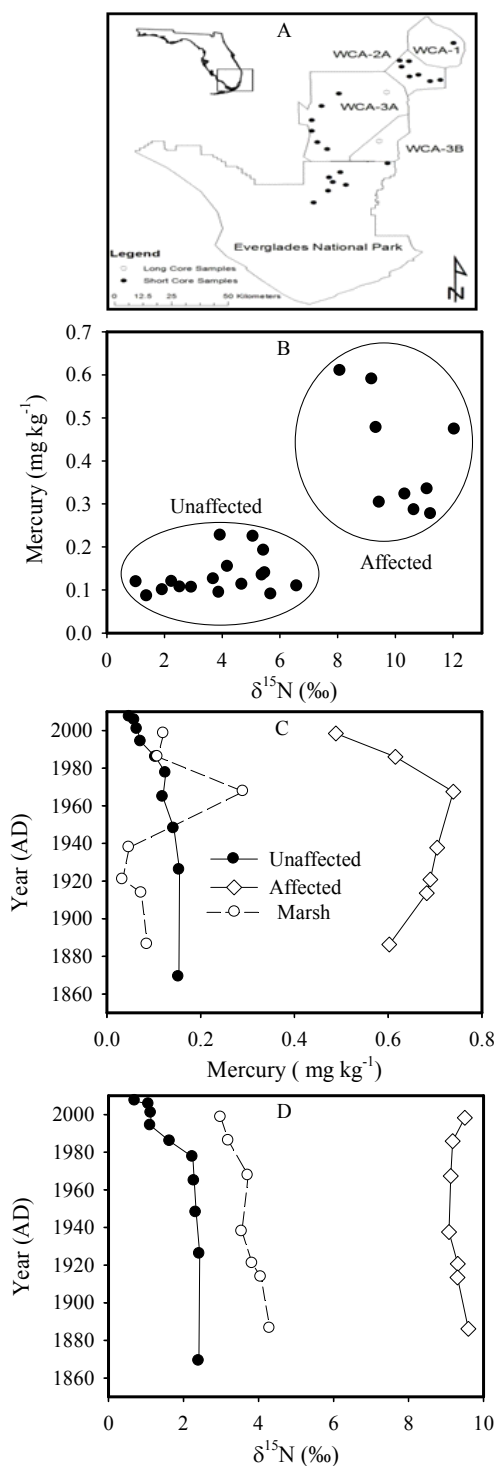


Figure 3B-12. Location of study sites in the EPA. Solid and open circles indicate sampling sites from surface (short cores) and deep soil (long cores) (A); soil THg concentrations plotted against soil $\delta^{15}\text{N}$, a proxy for wading bird influence (B); and historical changes in soil THg concentrations (C); and $\delta^{15}\text{N}$ values (D) from an unaffected (solid circle) and affected tree island (open diamond), and marsh near the affected island (open circle).

MERCURY AND METHYLMERCURY SOURCES TO THE EVERGLADES

STATEWIDE MERCURY TOTAL MAXIMUM DAILY LOAD PROJECT

Gregory White¹, Donald M. Axelrad¹ and Curtis D. Pollman²

As of 2010, all 50 U.S. states had fish consumption advisories in effect due to elevated fish Hg levels, and 81 percent of all advisories nationally were issued, at least in part, because of Hg contamination (USEPA, 2011). Similarly, in 2012 excessive Hg levels in fish were the leading cause of water quality impairment in Florida (FDEP, 2012b). Twenty species of Florida freshwater fish are under some level of advisory (i.e., recommendations of limited consumption or no consumption) including several species in the Everglades. The entire coast of Florida, including over 60 species of marine fish, is also under consumption advisory (FDOH, 2012).

Wet and dry atmospheric deposition of Hg to land and water bodies is the main Hg source to water bodies in Florida as well as the Everglades. Wet atmospheric deposition includes dissolved Hg and particulate Hg scavenged from the atmosphere during rainfall; and dry deposition includes particulate Hg removed from the atmosphere by gravitational settling and particle impaction, and gaseous Hg (predominantly reactive gaseous mercury) reacting with surfaces. For the Everglades, Hg is almost entirely (greater than 95 percent) sourced from wet and dry atmospheric deposition (Guentzel et al., 1998, 2001; Landing et al., 1995; Pollman et al., 1995; Stober et al., 1996, 1998a, 2001).

While a portion of the mercury present in the atmosphere is from natural sources, about 70 percent of the global mercury burden is from human activities that release mercury to the air (FDEP, 2012a). Hg sources to Florida's water bodies originate internationally as well as from U.S. and local sources. Florida's latitude, geographical setting, and meteorology allow a high rate of Hg deposition from the atmosphere onto Florida's lands and waters (Gu et al., 2012; FDEP, 2012a). Atmospheric Hg eventually deposits to land and water where a small proportion (<1–10 percent) is converted in water bodies to MeHg by naturally occurring bacteria and readily bioaccumulates up aquatic food chains, peaking in top predator fish (Gu et al., 2012). Almost all human exposure to MeHg results from eating fish (Sunderland, 2007), and there is a high risk of adverse health effects in children (e.g., neurodevelopmental deficits) from in utero MeHg exposures that result from women's consumption of fish with elevated MeHg levels (NRC, 2000; USEPA, 2012a).

FDEP rules classify water bodies as impaired for Hg pollution based on FDOH fish consumption advisories. The federal Clean Water Act requires states to submit to the USEPA lists of impaired waters and establish TMDLs for these waters. TMDLs define the maximum amount of a pollutant that a water body can assimilate without exceeding water quality standards—in this case, exceedances of the fish tissue MeHg criterion for protection of human health from consumption of fish. As such, development of TMDLs is an important step toward restoring impaired waters. The FDEP has established a draft statewide mercury reduction goal, or TMDL, to address excessive Hg levels found in some Florida fish (FDEP, 2012a). The statewide Hg TMDL project focuses on monitoring and modeling (Figure 3B-13). Atmospheric monitoring includes wet and dry concentrations of speciated mercury (Figure 3B-14). Dry deposition was monitored via continuous bi-hourly sampling for speciated mercury, continuous sampling of primary pollutants (O₃, SO₂, CO, NO, NO_y), filtered particulates PM_{2.5} and PM₁₀ (analyzed for trace elements, i.e., Mg, Al, P, S, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Rb, Sr, Mo, Cd, La, Ce, Sm, Pb), and continuous meteorology. Precipitation (wet deposition) was collected daily via

the University of Michigan's Automated Sequential Precipitation Samplers and analyzed for the same suite of trace elements, speciated mercury, mercury isotopes, and nutrients.

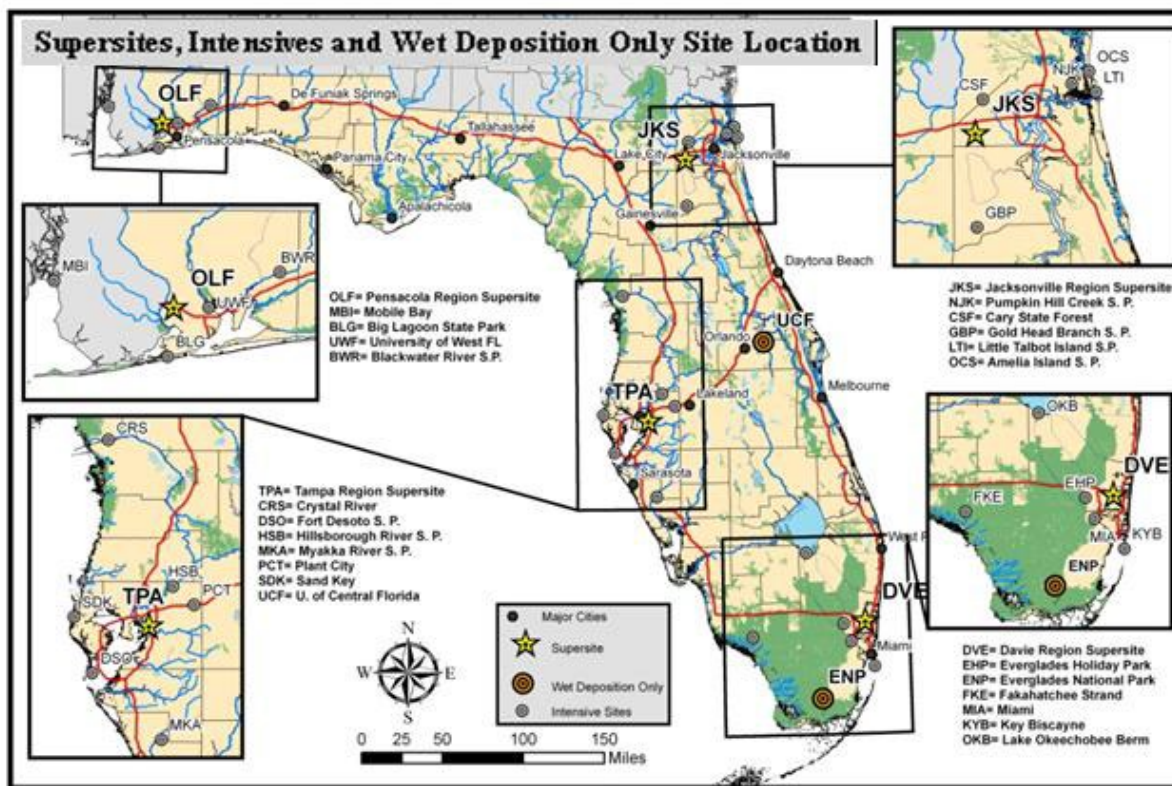


Figure 3B-13. Atmospheric monitoring locations for the statewide Hg Total Maximum Daily Load (TMDL) project.

Modeling evaluated two domains, atmospheric and aquatic systems. The dominant atmospheric sources, atmospheric chemistries, transport, and deposition were evaluated from a deterministic approach. The relationships within aquatic systems of water quality, sediment quality (lakes only), and THg in fish tissue were evaluated from an inferential approach. The atmospheric modeling to predict loads of Hg depositing in Florida was conducted at four scales using various public domain modeling software (**Table 3B-2**). The underlying code for each type of modeling software was enhanced during this project. The modeling effort employed pioneering details on sources and the most spatially temporarily resolute detail in Hg modeling to date.

Table 3B-2. Mercury modeling domains and software used for the statewide Hg TMDL project.

Spatial Domain	Mercury Chemistry Model	Meteorological Model	Spatial Resolution
Global	ECHMERIT	ECHMERIT & WRF	80 km
North America	CMAQ	WRF	36 km
Southeastern US	CMAQ	WRF	12 km
Florida	CMAQ	CMAQ & WRF	4 km

For the CMAQ modeling, all spatial domains used a pioneering tagging system to track 12 emission categories selected by the FDEP (e.g., coal-fired power plants, natural gas-fired power plants). This allowed for modeled deposition, both wet and dry, as well as mercury species to be identified with a tagged category. The modeling produced some of the most resolute and best evaluated outputs to date, with results showing a greater significance of dry deposition to the total mercury deposition onto Florida. Additionally, a greater variability in deposition spatial patterns was documented, with localized changes in distances of tens of kilometers.

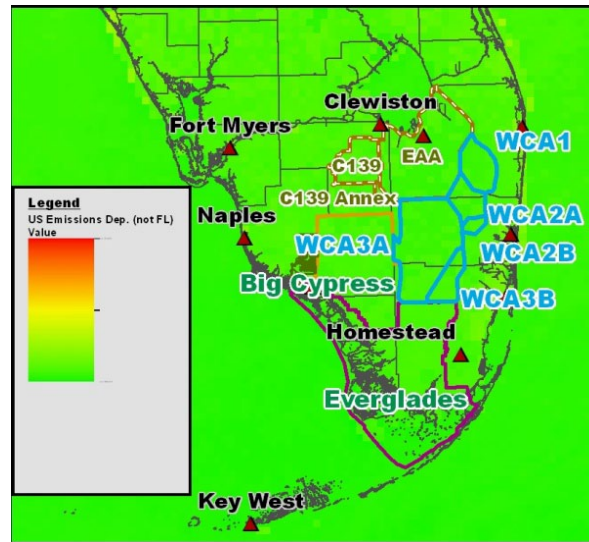
The source attribution tagging showed that the overwhelming fraction of Hg load was from out of state, with Florida sources typically contributing only 3 to 5 percent of total atmospheric deposition to a maximum percent contribution in the low teens. Loads from other southeastern states were identified as being significant sources and larger than Florida sources in north Florida. Statewide, sources external to the U.S. dominated the deposition loads. For the Everglades, mean atmospheric Hg deposition for 4 x 4 km grids in the EPA from global sources (outside of Florida and the U.S.) ranged from 95 to 99 percent for wet deposition and from 88 to 98 percent for dry deposition as a percentage of total atmospheric deposition. For the EPA, dry to wet deposition was about 30:70 (Sanford Sillman, University of Michigan, pers. comm.). **Figure 3B-14** depicts modeled Hg deposition for nationwide-sourced (non-Florida; panel A), Florida-sourced (panel B), and global-sourced (international; panel C) total wet and dry mercury atmospheric deposition.

Deposition modeling conducted previously by several researchers produced results that are consistent with the new University of Michigan estimates; these also suggest that sources originating from outside of North America are the dominant sources of atmospheric Hg deposited in the Everglades. For example, Seigneur *et al.* (2003) suggests that only 17 percent of the total mercury deposition in the Everglades originates from within North America. Subsequent modeling reported by Carlton *et al.* (2004) using the same model but at a finer scale of spatial resolution (20 x 20 km versus Seigneur's 100 x 100 km grid) yielded North American contributions of 8 percent for the Everglades. More recently, modeling conducted using REMSAD coupled with inputs averaged from three different global scale models indicated approximately 90 percent of the Hg deposited in the Everglades originates from outside the REMSAD model domain (which includes the continental U.S. and parts of Mexico and Canada) (USEPA, 2008; D. Atkinson, pers. comm., May 2009). Clearly, significantly reducing mercury sources to the Everglades will require reduction of global sources via mechanisms such as international treaties although this is not likely in the near term.

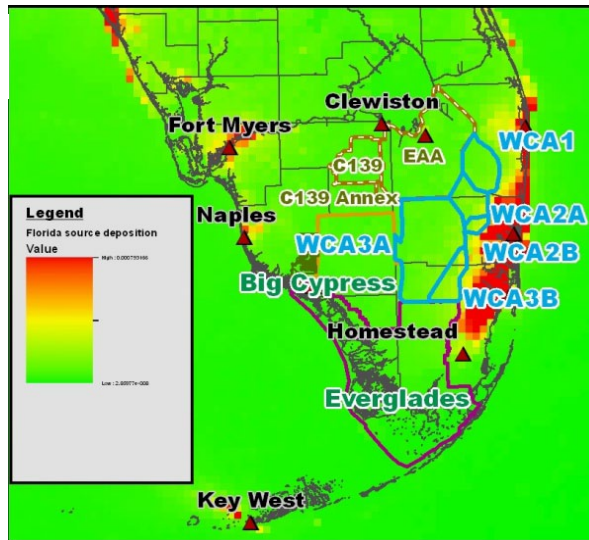
The aquatic modeling applied inferential statistics to the water quality, sediment quality, and fish tissue monitoring data collected from 2008–2010. This effort developed relationships of constituents to have statistical models to better predict THg in fish tissue and sought to produce statistical models that could be applied to assess necessary load reductions for fish tissue to meet FDEP-identified target values for LMB. A market basket approach—considering the broad variety of fish species Floridians consume—was used to determine reductions in mercury sources necessary to achieve a 90 percent certainty of not exceeding the MeHg reference dose from consuming fish. This analysis determined that Florida fish MeHg levels would need to be reduced by 60 percent to achieve the protective target MeHg level. This reduction in total sources (natural and anthropogenic) is equivalent to an 86 percent reduction in anthropogenic sources given that natural background is assumed to be 30 percent of the total mercury source to the atmosphere. The 86 percent reduction in mercury sources is needed for all nonpoint (atmospheric) Hg sources (from Florida, other U.S. States, and other countries) to protect public health in Florida.

577

A



B



C

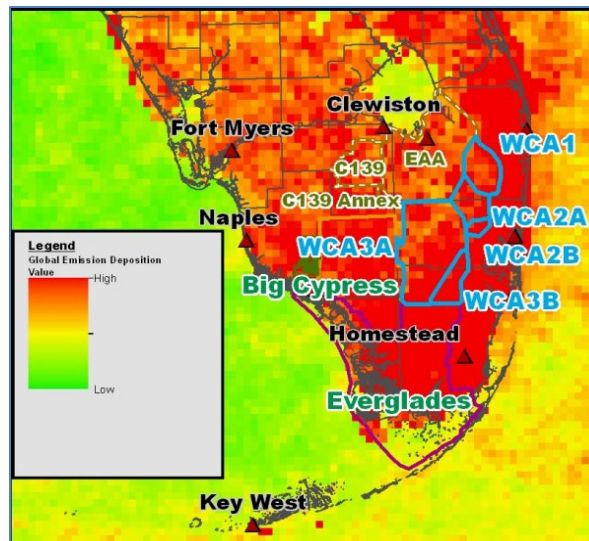


Figure 3B-14. Modeled Hg deposition for national-sourced (non-Florida sourced; A), Florida sourced (B), and global-sourced (C) total wet and dry mercury atmospheric deposition.

MAJOR SOURCES AND SINKS OF METHYLMERCURY IN THE EVERGLADES

Yanbin Li¹² and Yong Cai¹³

Hg methylation and MeHg demethylation have been found to occur in various compartments of the Everglades, including soils (Gilmour et al., 1998; Vaithyanathan et al., 1996), floc (flocculent materials on top of soil) (Marvin-DiPasquale and Oremland, 1998), periphyton (Cleckner et al., 1999), and water (Li et al., 2010). However, it is still unclear which compartment is the major source or sink due to the lack of estimation and comparison of the net MeHg production or degradation in these areas. This information void is partially due to defects in previous models used to estimate the net production of MeHg, which have limited understanding of mercury cycling. This study investigates mercury methylation/demethylation in various compartments of the EPA, assesses the role of these processes in the spatial distribution of MeHg, and identifies major sources and major sinks of MeHg in this ecosystem (Li et al., 2012).

To achieve these objectives, double stable isotope (¹⁹⁹Hg²⁺ and Me²⁰¹Hg) addition experiments were conducted to study methylation/demethylation of mercury in various compartments and areas of the EPA. The net production or degradation rates of ambient and newly input Hg were calculated in soil, periphyton, floc, and water of the EPA using improved calculation models. The previous models for estimating these parameters were improved by taking into account the differences between newly input and ambient mercury in methylation/demethylation efficiency, and correcting the contribution of photodemethylation to Me¹⁹⁹Hg concentration when calculating methylation rates in water.

Significant methylation and demethylation of mercury were observed in soil, floc, and periphyton. Methylation and demethylation, which are mediated by sunlight, occurs in Everglades waters. However, the rate of Hg photomethylation [$1.14 \pm 0.02 (\times 10^{-4} \text{ d}^{-1})$] was much slower than that of MeHg photodemethylation ($k_d = 0.26 \pm 0.04 \text{ d}^{-1}$), indicating that methylation in water plays a minor role in the cycling of MeHg in the Everglades region. Although the newly input Hg²⁺ has a much higher methylation/demethylation efficiency, the net daily produced MeHg from this source was found to account for a very small fraction of MeHg produced (i.e., less than 0.4 percent of that produced from ambient Hg).

Soil was estimated to be the largest source of MeHg in all four areas of the EPA, accounting for 98–100 percent of totally produced MeHg. The net MeHg production rate in soil ranged from 418 to 6,238 ng m⁻² d⁻¹, in the order of Refuge < WCA-2 < WCA-3 < ENP (**Figure 3B-15**). Floc is a major sink of MeHg, with a degradation rate of -9 to -145 ng m⁻² d⁻¹. Water is another sink for MeHg, accounting for approximately 2–10 percent of the total MeHg degradation. Periphyton was found to be a source for MeHg in the northern EPA (Refuge and WCA-2), and a sink in the southern EPA (WCA-3 and ENP).

There is a significant difference between the ambient and newly input Hg species in methylation/demethylation efficiency. The ratio of methylation rate constant of ambient to newly spiked Hg and the ratio of demethylation rate constant of ambient to newly spiked MeHg were estimated to be 0.06 and 0.93 in soil, 0.02 and 0.71 in floc, and 0.53 and 0.50 in periphyton, respectively. If this difference was not included in the estimation model, then there would be significant error. For example, the estimated net production (or degradation) rate of MeHg in soil

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could be overestimated by a factor of 20. The average of the estimated net production (or degradation) rate of MeHg in floc would increase from -70 to $600 \text{ ng m}^{-2} \text{ d}^{-1}$. These results indicate that their differences must be considered when estimating the net production of MeHg.

Additionally, statistical analyses indicate that spatial distribution of MeHg in soil and periphyton are mainly related to their in situ methylation. Both methylation and demethylation of mercury in floc are important for controlling MeHg concentration in this compartment, while water MeHg concentration may be controlled by methylation in periphyton and photodemethylation in water column.

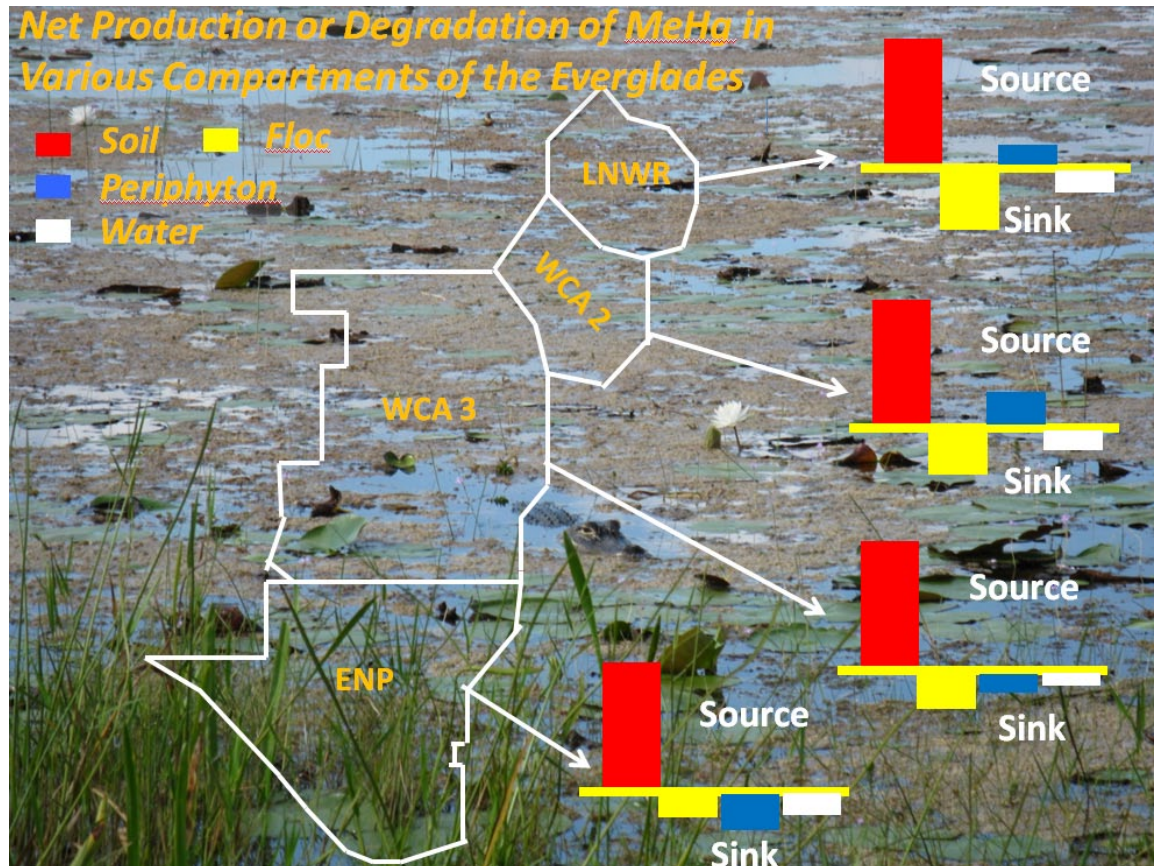


Figure 3B-15. Net production or degradation of MeHg in soils, floc, periphyton, and water across the EPA.

MERCURY AND SULFUR BIOGEOCHEMISTRY

AQUATIC CYCLING OF MERCURY IN THE EVERGLADES DATABASE AVAILABILITY AND INITIAL ANALYSES

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G.S. Riedel¹⁵ and David P. Krabbenhoft¹⁹

Between 1995 and 2008, the Aquatic Mercury Cycling in the Everglades (ACME) Project examined in detail the biogeochemical parameters that influence MeHg production at sites across the Everglades. The interdisciplinary ACME team studied mercury cycling in the Everglades through a process-based, biogeochemical lens (Hurley et al., 1998). The ACME database, available at the USGS South Florida Information Access (SOFIA) web page (<http://sofia.usgs.gov/exchange/acme/introduction.php>), comprises data from all ACME researchers in one central dataset (presently, 61 parameters and 281 sites) to promote its use by interested stakeholders. This website allows download of biogeochemical field data from the ACME study. Data are available in tab-delimited or comma-separated value text format, which can be imported into Excel or most spreadsheet or database programs. Data may be selected by station, water quality parameter, or date.

Using the ACME database, Gilmour et al. (2012) provide a detailed biogeochemical evaluation of set of 10 study sites in the EPA (**Figure 3B-16**) located across the nutrient, sulfur, and dissolved organic matter (DOM) gradients of the Everglades marsh ecosystem. Spatial and temporal trends in THg and MeHg in concentrations in surface water, near-surface sediment, and porewater are presented. Biogeochemical information on the study sites is also covered, with a focus on sulfur, DOM, and soil microbiology including microbial metabolic rates and rate constants for Hg methylation. Relationships among inorganic mercury, MeHg, and the other biogeochemical variables across the ecosystem and more than 13 years of data collection are examined.

The ACME study was designed to evaluate the biogeochemical controls on net MeHg in this ecosystem that appear particularly sensitive to mercury inputs. The program sought to determine the importance of mercury methylation in controlling MeHg levels in biota in the Everglades and understand factors such as water chemistry, hydroperiod, and inorganic mercury, nutrient, and sulfur loading that, in turn, control the methylation process in this wetland. Key findings of this study include the following:

- There are large gradients in sulfur, MeHg, and DOM across the Everglades ecosystem, driven in part by agricultural drainage and water management practices.
- Sulfate loading to the Everglades increases microbial sulfate reduction in soils, leading to more reducing conditions, greater cycling of nutrients in soils, production of toxic

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¹⁹ U.S. Geological Survey, Middleton, WI

sulfide, and enhanced MeHg production and bioaccumulation in some parts of the regional ecosystem.

- Sulfate loading and peat degradation are linked processes that lead to increased concentrations and reactivity of DOM in the impacted areas. In turn, this highly reactive DOM also enhances MeHg production.

Figure 3B-17 is an example of analyses conducted in Gilmour et al. (2012) using the ACME database. Across all the sites and dates sampled, MeHg as a percent of THg in surface waters increases with surface water sulfate up to a maximum, and then declines. This is suggestive of the “Goldilocks” or unimodal MeHg and sulfate response - despite the confounding effects of varying water and soil chemistry across the 10 EPA study sites - very low sulfate results in low MeHg production as does very high sulfate (due to associated high sulfide).

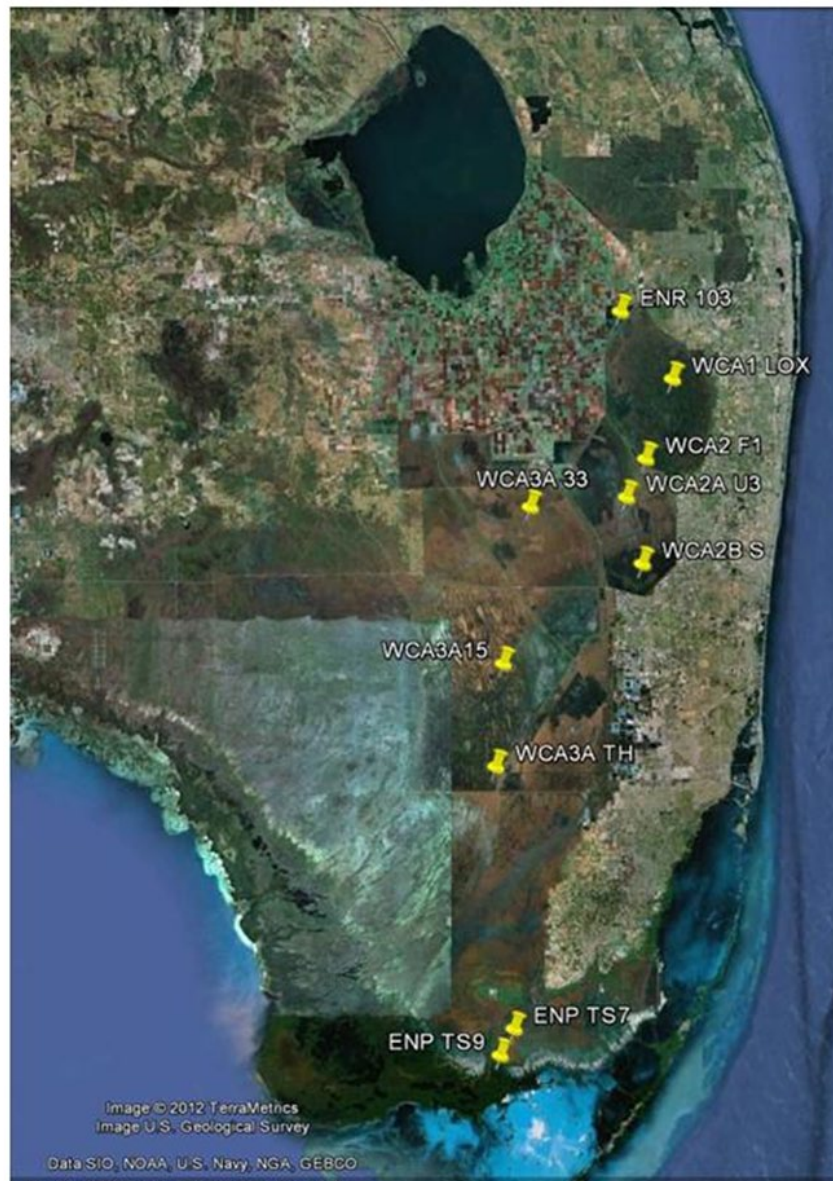


Figure 3B-16. Location of the 10 Aquatic Mercury Cycling in the Everglades (ACME) study sites in the EPA.

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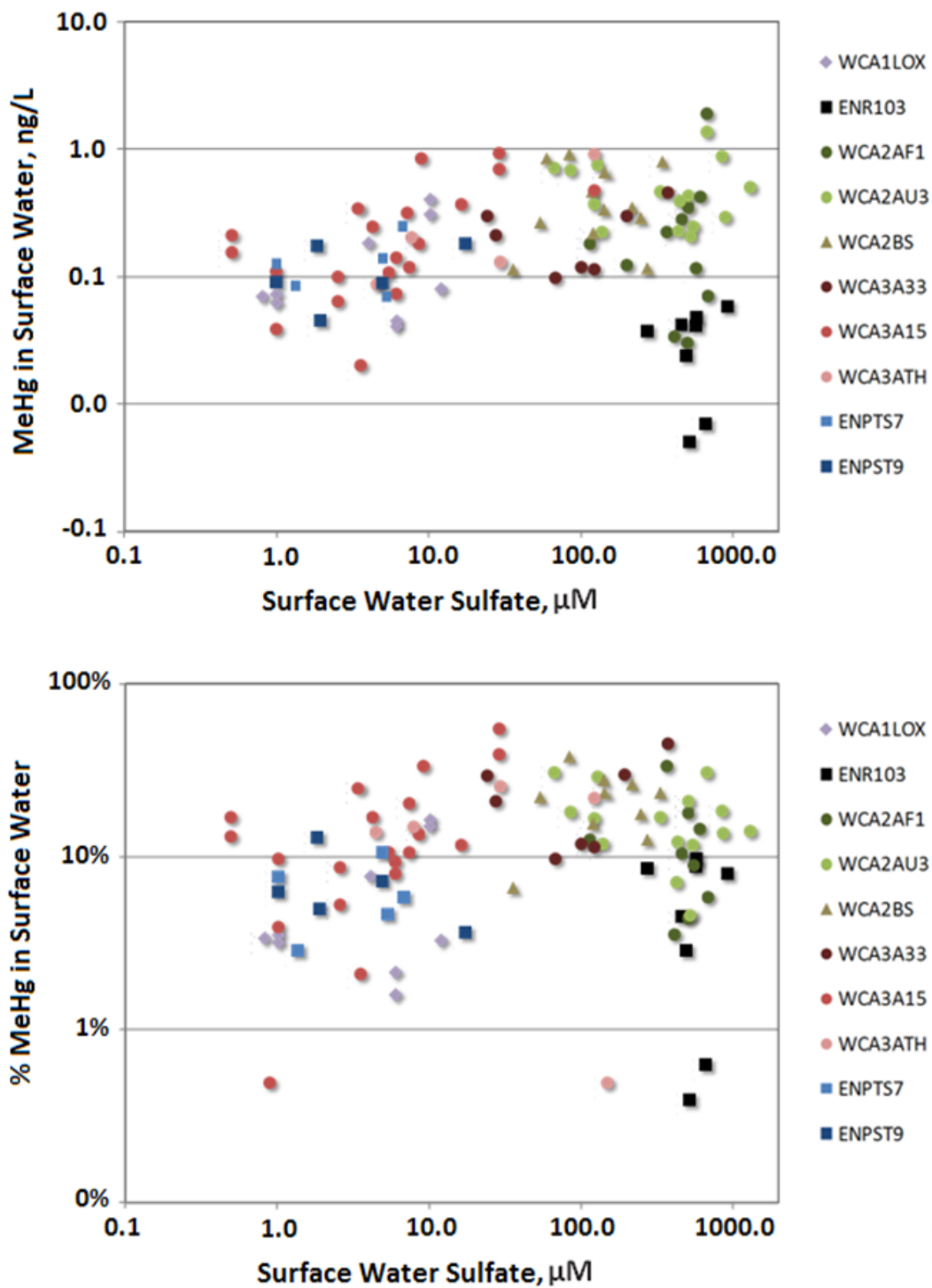


Figure 3B-17. Relationship between MeHg (top) and MeHg as percent of %THg (bottom) and surface water sulfate (SO_4^{2-}) across 10 ACME study sites and all dates.

MODELING SULFATE AND *GAMBUSIA* MERCURY RELATIONSHIPS IN THE EVERGLADES

Curtis D. Pollman²

Mercury is problematic because methylation in freshwater aquatic ecosystems converts inorganic mercury to its more bioaccumulative and toxic form, MeHg. MeHg production is governed in part by the activity of sulfate-reducing bacteria (SRB) that use sulfate (SO_4^{2-}) as the terminal electron acceptor to metabolize organic matter under anaerobic conditions (Gilmour et al., 1992; Branfireun et al., 2001; Jeremiason et al., 2006). In the Everglades, studies conducted using intact soil cores have demonstrated that mercury methylation is enhanced by additions of SO_4^{2-} into the water column depending upon ambient concentrations (see Gilmour, 2011). Further support for the role of SO_4^{2-} in the Everglades is indicated by correlation analyses that link long-term dynamics of mosquitofish Hg concentrations to the dynamics of SO_4^{2-} concentrations in the water column at site 3A-15 within WCA-3A (D. Krabbenhoft, unpublished data; Axelrad et al., 2005).

Gilmour and Henry (1991) hypothesized that the relationship between sulfate and inorganic mercury methylation rate was nonlinear and essentially unimodal, with a water column SO_4^{2-} concentration in the range of 200–500 mM (~20–50 mg/L) supporting maximal rates of methylation (**Figure 3B-18**). According to this paradigm, SO_4^{2-} availability at concentrations below the optimal concentration limits the activity of sulfate-reducing bacteria (SRB), which in turn limits rates of methylation. At concentrations above the optimum, sulfate reduction produces sulfide at levels inhibitory to inorganic mercury methylation, primarily through the sequestration of labile Hg^{2+} , which is a necessary substrate to support methylation. In a recent review of the literature devoted to studies on the relationship between sulfur and mercury methylation, Gilmour (2011) suggests that the optimal concentration of SO_4^{2-} in the water column supporting methylation in freshwater ecosystems is lower (~100 mM , or 10 mg/L), although it can vary depending upon sulfide levels.

Pollman (2012b) recently used data on *Gambusia* Hg and water column SO_4^{2-} concentrations collected from marsh sites throughout the EPA as part the USEPA's Regional Monitoring and Assessment Program (REMAP; Scheidt et al., 2000; Scheidt and Kalla, 2007) in an effort to identify whether the sulfate maximum, widely hypothesized (e.g. Gilmour (2011) exists for the Everglades. Pollman used 90th percentile *Gambusia* Hg concentrations to define the “maximum methylation potential” as a function of SO_4^{2-} concentrations, with SO_4^{2-} concentrations divided into intervals for the purposes of determining the 90th percentile *Gambusia* Hg concentration. As shown in **Figure 3B-19**, study results indicate a unimodal response similar to that originally hypothesized by Gilmour and Henry (1991). The maxima of the maximum methylation potential curves varied between regions sampled by the REMAP and may reflect the amount of sulfide that accumulates as sulfate reduction proceeds (Gilmour, 2011). However, it should be noted that *Gambusia* Hg cannot be predicted by sulfate concentrations alone, since other factors such as DOM, Hg availability and dietary composition of fish are also very important factors in determining Hg in fish. It is also interesting to note that the maxima for all the regions were nearly identical with the exception of WCA-2, and may reflect differences in the nature and concentrations of dissolved organic carbon (DOC), which in turn can influence the bioavailability of Hg^{2+} (Gilmour, 2011). The SO_4^{2-} concentrations corresponding to the maximum methylation potential varied from approximately 1.6 mg/L (1–2.7 mg/L at WCA-3) to 33 mg (20–55 mg/L at the Refuge). When the *Gambusia* data are integrated across all four sampling regions used by the REMAP, the maximum methylation potential occurs at SO_4^{2-} concentrations of approximately 4 to 5 mg/L .

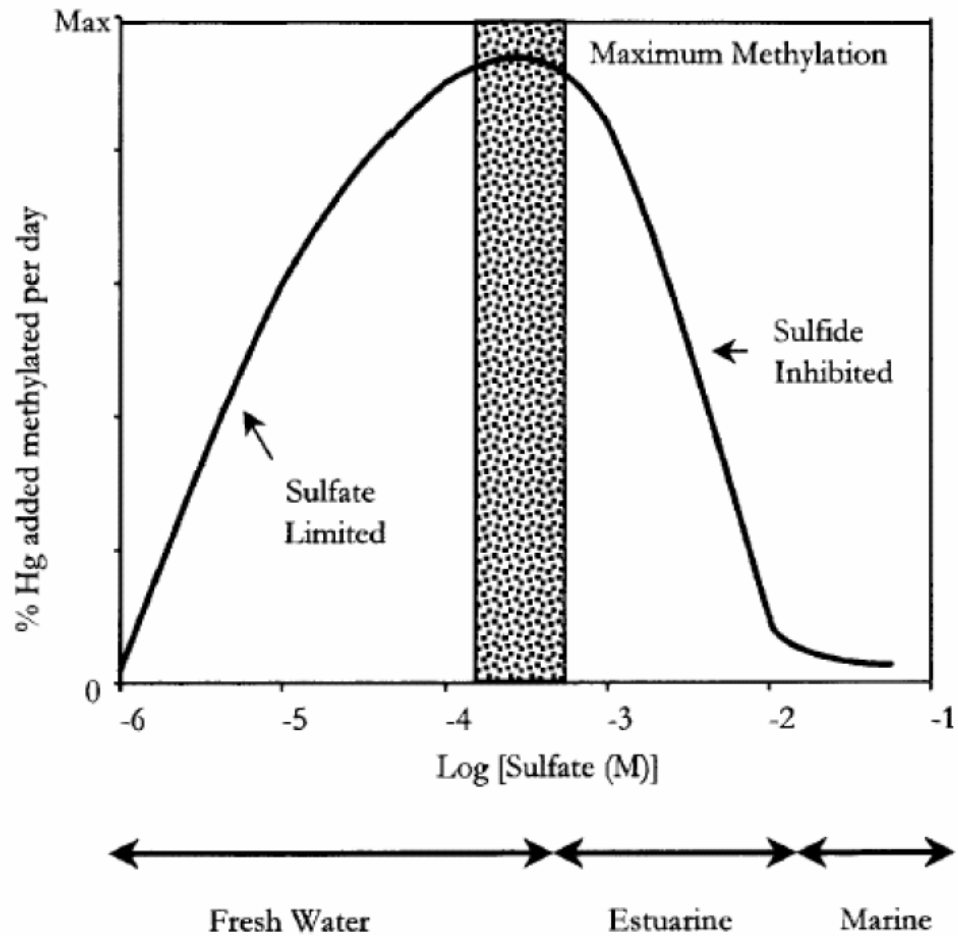


Figure 3B-18. Theoretical relationship between water column SO_4^{2-} and Hg methylation rates in sediments hypothesized by Gilmour and Henry (1991); figure as redrawn by Langer et al 2001.

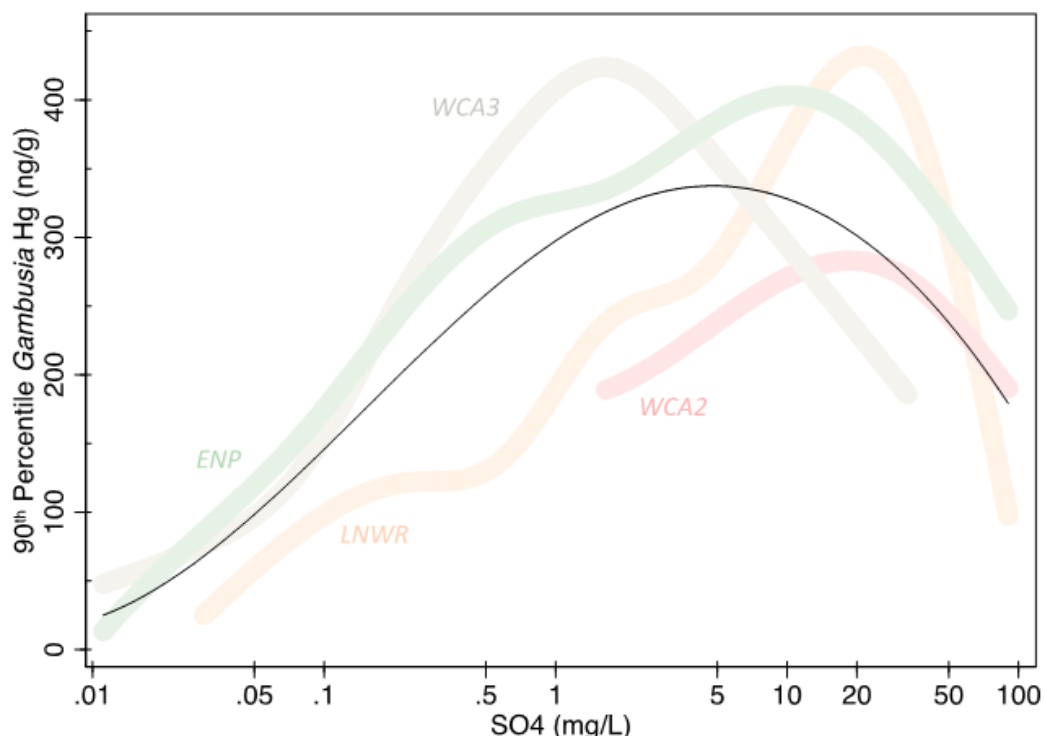


Figure 3B-19. Variations in SO_4^{2-} methylation potential as determined by changes in *Gambusia* Hg concentrations as a function of ambient water column SO_4^{2-} concentrations. Curves are the result of cubic splines constructed using the 90th percentile *Gambusia* Hg concentration for *ln*-transformed SO_4^{2-} concentration intervals [each interval encompasses 1 *ln* unit change in concentration, with the first interval starting at -6 (0.002 mg/L)]. The black curve shows the sulfate methylation potential resulting from aggregating data from all four regions of the EPA together. Data are from USEPA REMAP Cycles 0–6; analysis from Pollman (2012b).

Given both the theoretical and empirical links between SO_4^{2-} and Hg methylation, and given that SO_4^{2-} concentrations throughout much of the Everglades are enriched anthropogenically, one potential option for mitigating high Hg concentrations in fish would be through controlling SO_4^{2-} inputs to the Everglades. However, the role of SO_4^{2-} in the biogeochemical cycling of Hg within the Everglades is complex and confounded by other variables, and these complexities must be understood and quantified before an effective strategy that includes SO_4^{2-} controls for resolving the Hg problem can be designed and implemented. For example, high SO_4^{2-} concentrations can reduce Hg methylation rate through the evolution of high concentrations of sulfide and subsequent precipitation of dissolved Hg^{2+} as metacinnabar (Aiken et al., 2011a)— Hg^{2+} being the necessary precursor for MeHg production. Therefore, the relationship between SO_4^{2-} concentrations and Hg methylation is non-linear and unimodal (Gilmour and Henry, 1991). Moreover, the influence of other variables—particularly those related to trophic state—can dominate the expression of Hg in the food chain. As a result, simple correlation studies that attempt to link Hg concentrations in *Gambusia* throughout the Everglades fail to show a clear and meaningful relationship. Restated, mercury biogeochemical cycling is influenced by a number of variables and, as a result, simple models that try to relate biota mercury concentrations to variations in a single variable such as sulfate in a system as biogeochemically diverse as the Everglades will be able to capture only a fraction of the variability. It is important to note that these complexities do not negate the importance of sulfate, but do require that analyses that evaluate the mitigative benefits of controlling sulfate on biota mercury concentrations include effects of variations in other key process variables across the landscape as well.

Because the relationship between SO_4^{2-} concentrations and methylation is hypothesized to be unimodal, the effect of management strategies to reduce SO_4^{2-} concentrations across the Everglades may result in decreases in biota Hg concentrations in some locations but increases in other areas. Such results were indicated by preliminary modeling efforts conducted by Pollman (unpublished data) with the USEPA Regional Environmental Monitoring and Assessment Program (R-EMAP) database²⁰ (Scheidt and Kalla, 2007), in which reducing SO_4^{2-} concentrations by a nominal amount (e.g., 50 percent) did not equate to equivalent reductions in *Gambusia* Hg concentrations and that the expected response (both magnitude and direction) varied spatially. As a result of the complexities in the SO_4^{2-} -Hg methylation relationship, the key objectives of this study were to:

- Better characterize the non-linear relationship between SO_4^{2-} and maximum methylation potential, using R-EMAP data for *Gambusia* and SO_4^{2-} concentrations for all eight cycles of data available;
- Incorporate the algorithm for SO_4^{2-} effects on methylation potential in a statistical model framework that, when developed in conjunction with other key water column and sediment chemistry variables, can be used to predict variations in *Gambusia* Hg concentrations across the EPA both spatially and temporally;

²⁰ The marsh component of the Everglades R-EMAP was implemented in 1995 by the USEPA to evaluate the health of the Everglades marsh ecosystem. R-EMAP utilized a stratified, randomized approach towards sampling that was designed to facilitate quantitative estimates of the areal distribution and variability of a broad suite of key ecosystem metrics, including nutrients, components of major ion chemistry (including SO_4), and Hg concentrations in biota (including *Gambusia*), sediments, and surface water. Sampling of the Everglades marsh was conducted in three phases as a series of cycles, with each cycle corresponding to either the dry or wet hydroperiod. Phase I sampling was conducted during both 1995 (Cycles 0 and 1) and 1996 (Cycles 2 and 3), Phase II sampling was conducted during 1999 (Cycles 4 and 5), and Phase III sampling was conducted during 2005 (Cycles 6 and 7).

- Evaluate and analyze changes in water chemistry and *Gambusia* Hg concentrations over time at proximally located stations to help identify what factors appear to be driving observed decreases in *Gambusia* Hg documented in the R-EMAP datasets between 1995 and 2005;
- Develop a regional conceptual model of SO_4^{2-} dynamics that predicts how SO_4^{2-} concentrations will change across the Everglades based on atmospheric deposition, hydrologic inputs and SO_4^{2-} export from the EAA, and connate seawater intrusion in the major canals; and
- Predict changes in the spatial and overall distribution of *Gambusia* Hg concentrations as a function of specified changes in SO_4^{2-} export from the EAA with other variables held constant.

Impacts of Reducing Sulfate Concentrations in Everglades Agricultural Area Discharge Waters

SO_4^{2-} inputs to the EPA include three primary sources: (1) direct inputs from atmospheric deposition, (2) likely inputs of connate seawater²¹ into the canals draining the EAA and routing of water through the EPA, and (3) export of otherwise “excess” SO_4^{2-} from the EAA derived from other sources, including sulfur that was originally applied as a soil amendment, SO_4^{2-} released from soil oxidation within the EAA, and elevated SO_4^{2-} concentrations associated with water pumped from Lake Okeechobee and passing through the EAA.

The objective of this recent study was to evaluate the efficacy of reducing this latter excess or non-marine SO_4^{2-} exported from the EAA as a means of reducing fish tissue Hg concentrations throughout the Everglades (Pollman, 2012b). Model building, analyses of temporal trends, and impacts of SO_4^{2-} management scenarios were conducted using *Gambusia* Hg data coupled with ambient water and sediment chemistry collected by the USEPA throughout the Everglades as part of R-EMAP sampling conducted between 1995 and 2005 (Stober et al., 1998b; Scheidt et al., 2000; Scheidt and Kalla, 2007). Four different scenarios of SO_4^{2-} reductions were simulated using the SO_4^{2-} dynamics model coupled with the statistical *Gambusia* Hg model. The scenarios were designed to examine reductions in SO_4^{2-} exported from the EAA attributable to non-marine sources, with reductions in this “excess” SO_4^{2-} ranging from 25 to 100 percent.

The simulations suggest that eliminating the excess or non-marine SO_4^{2-} will reduce median SO_4^{2-} concentration across the EPA by about two-thirds (from approximately 2.4 to 0.8 mg/L). However, because of the nonlinear relationship between ambient SO_4^{2-} concentrations and Hg methylation potential, reductions in excess (non-marine) SO_4^{2-} , depending upon a sites initial SO_4^{2-} concentrations and the relative influence of waters from the EAA on ambient SO_4^{2-} levels, will result in increases in *Gambusia* Hg concentrations at some EPA locations and decreases at other areas. In addition, the overall shifts in *Gambusia* Hg concentrations are expected to be small, regardless of the magnitude in reduction in excess (non-marine) SO_4^{2-} . Based on the underlying assumptions of the analysis used to quantify the magnitude of connate seawater input, this is because the overall impact of SO_4^{2-} exiting the EAA not only reflects excess (non-marine) SO_4^{2-} that likely originates in large part from sulfur applied as a soil amendment (including other

²¹ Connate seawater generally refers to groundwater in the surficial aquifer that is marine in origin and was trapped in the interstices of the limestone as the geologic material was deposited. The export of major ions that are ultimately marine in origin may also reflect continued flushing of saline residues present in the muck soils and rock of the EAA (Chen et al., 2006). At this time, it is not possible to distinguish between either pathway; in this report, connate seawater refers a relict marine source that is present either in the surficial aquifer, EAA soils, or both.

agricultural inputs draining into the Kissimmee River and Lake Okeechobee) and SO_4^{2-} released from soil oxidation within the EAA, but also SO_4^{2-} derived from connate seawater.

If the role of connate seawater as a source of SO_4^{2-} is indeed as large as suggested by this analysis, then the magnitude of either source alone (connate seawater or non-marine SO_4^{2-} exiting the EAA) is sufficient to elevate concentrations of SO_4^{2-} through much of the EPA by well over an order of magnitude compared to expected background levels. A critical component underlying the SO_4^{2-} reduction scenario analyses was the assumption that chloride (Cl^-) concentrations in the major canals draining the EAA primarily reflect marine or connate seawater inputs. Support for this assumption is provided by an in-depth analysis of ion ratios and flow/concentration dynamics in the two major inflows discharging from the EAA into the northern EPA, although this assumption needs to be further tested. For example, whether the use of soil amendments within the EAA have influenced Cl^- concentrations appreciably in excess of connate seawater contributions is not clear but, based on the analyses conducted as part of this study, the likelihood that such amendment use exerts a large influence on Cl^- and sodium (Na^+) chemistry in the major canals appears unlikely.

Scenario Analyses – Results and Discussion

Four different scenarios of SO_4^{2-} reductions were simulated, corresponding to 25, 50, 75, and 100 percent reductions in excess (non-marine) SO_4^{2-} concentrations exported from the EAA. The effects of two scenarios (50 and 100 percent) on the distribution of SO_4^{2-} across the Everglades landscape are shown in **Figure 3B-20**. **Table 3B-3** indicates that eliminating excess or non-marine SO_4^{2-} from waters exported from the EAA is predicted to reduce the median SO_4^{2-} concentration across the EPA from 2.42 to 0.78 mg/L, and shows predicted negligible changes (*D*) in median *Gambusia* Hg concentrations for the EPA relative to predicted current levels for the four reduction scenarios for the non-marine SO_4^{2-} signal exported from the EAA.

Table 3B-3. Predicted changes in median SO_4^{2-} and *Gambusia* Hg concentrations in response to fractional reductions in the excess non-marine SO_4^{2-} signal exported from the EAA. Current *Gambusia* Hg concentrations are based on simulations conducted using ambient SO_4^{2-} levels for R-EMAP Cycles 6 and 7.

Metric	% Reduction in non-marine SO_4^{2-} signal exported from the EAA				
	Current	25%	50%	75%	100%
Median <i>Gambusia</i> Hg (ng/g)	83.3	83.2	86.1	85.8	85.7
Median SO_4^{2-} (mg/L)	2.42	2.03	1.62	1.20	0.78
Median <i>D</i> <i>Gambusia</i> Hg (ng/g)		-0.6	-1.5	-3.2	-5.7
Maximum <i>Gambusia</i> decrease (ng/g)		-4.5	-9.9	-16.2	-27
Maximum <i>Gambusia</i> increase (ng/g)		7.3	11.4	15.6	19.8

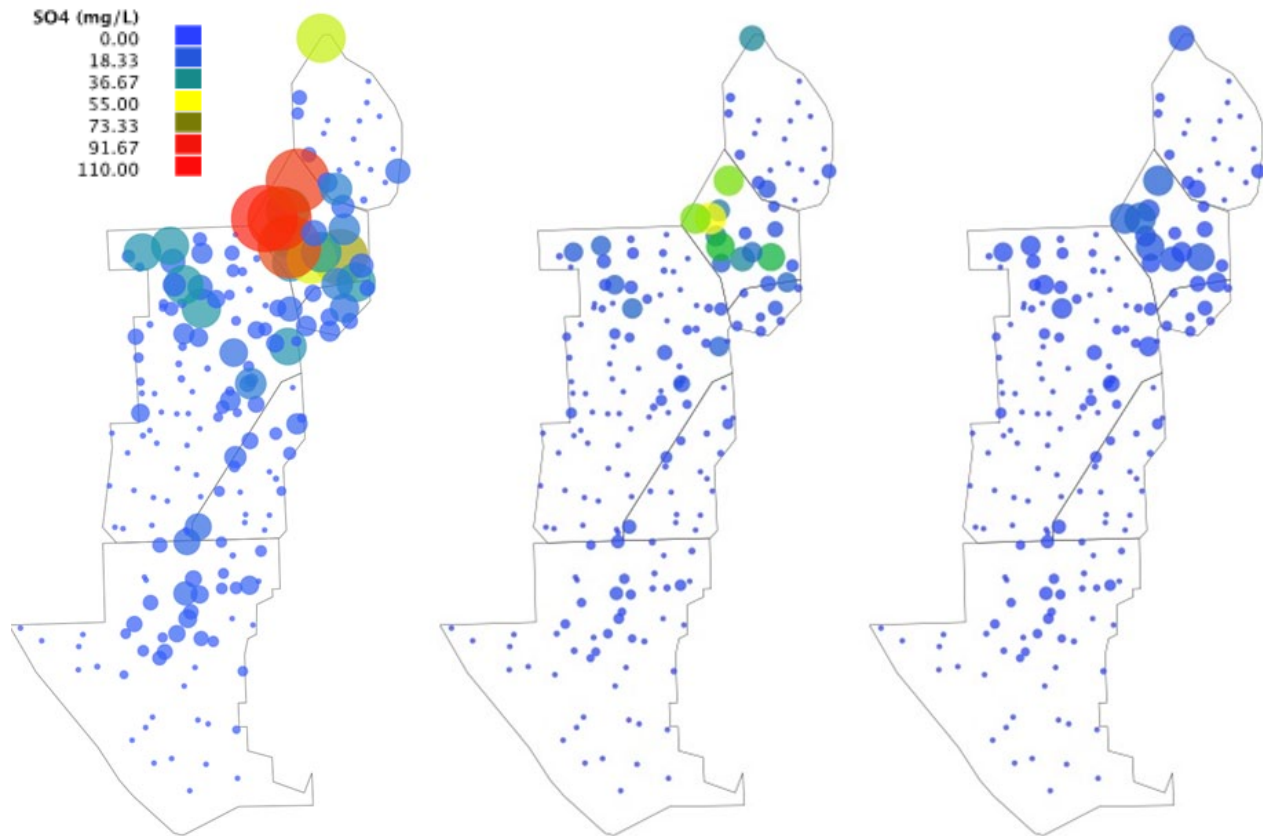


Figure 3B-20. Observed SO_4^{2-} concentrations (left) and predicted SO_4^{2-} concentrations assuming 50 and 100 percent reductions in the excess (non-marine) SO_4^{2-} component of concentrations exported from the EAA (middle and right, respectively) in the EPA during R-EMAP Cycles 6 and 7 (May and November 2005, respectively). [Note: These most current data were selected for scenario analyses because *Gambusia* Hg concentrations have decreased over the time period that R-EMAP sampling was conducted.]

Although the average or median shift in *Gambusia* Hg concentrations is predicted to be small for the 25 to 100 percent non-marine SO_4^{2-} reduction scenarios, larger reductions in SO_4^{2-} are expected to result in larger shifts—both positive and negative—in regions where the current SO_4^{2-} concentrations are near the maximum methylation potential. From a spatial perspective, the effect of reducing excess EAA SO_4^{2-} inputs is predicted to result in shifting Hg hotspots northward towards the EAA. This is illustrated by **Figure 3B-21**, which shows the spatial distribution of *DGambusia* Hg concentrations for the 50 and 100 percent reduction scenarios. Because ambient concentrations of SO_4^{2-} lie on both sides of levels corresponding to the maximum methylation potential, both WCA-3 and WCA-2 are predicted to undergo a change in *Gambusia* Hg concentrations in both directions. The largest magnitude of change in *Gambusia* Hg concentrations are predicted to occur in WCA-3, while shifts in WCA-2 are expected to be generally lower because of the larger, direct impact of EAA discharges on WCA-2 Cl^- and SO_4^{2-} concentrations. Hg concentrations in *Gambusia* throughout the ENP are expected to decline in response to reductions in excess (non-marine) SO_4^{2-} exports from the EAA of 50 percent or more. Based on the assumption that Cl^- is a valid tracer for connate seawater, the magnitude of either source alone (connate seawater or non-marine SO_4^{2-} exiting the EAA) is sufficient to elevate concentrations of SO_4^{2-} through much of the EPA by well over an order of magnitude compared to expected background levels. The contributions of both sources to median SO_4^{2-} concentrations in each major hydrologic unit, as well as expected background SO_4^{2-} concentrations are depicted on **Figure 3B-22**.

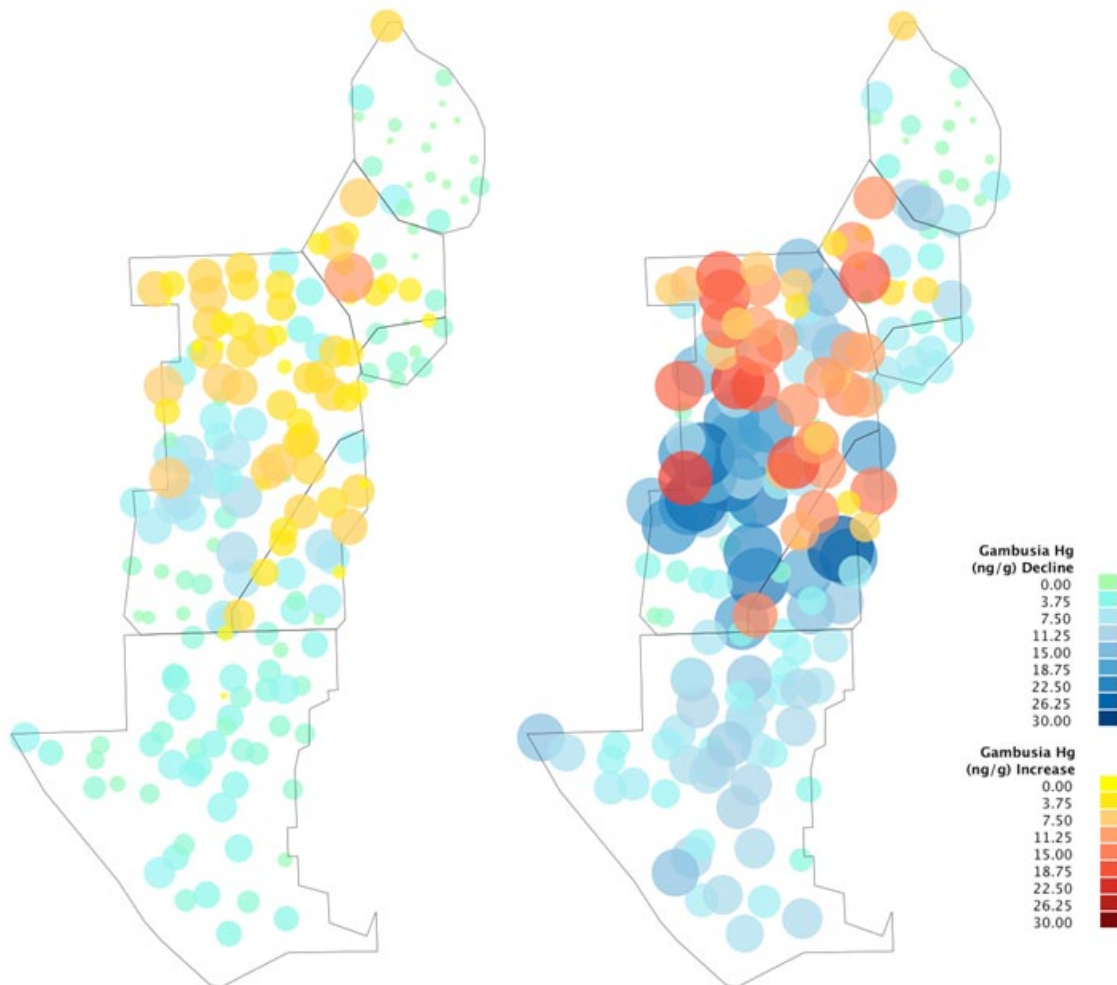


Figure 3B-21. Predicted changes in *Gambusia* Hg concentrations in response to 50 and 100 percent reductions in excess (non-marine) SO_4^{2-} exported from the EAA (left and right, respectively) using R-EMAP Cycles 6 and 7 data.

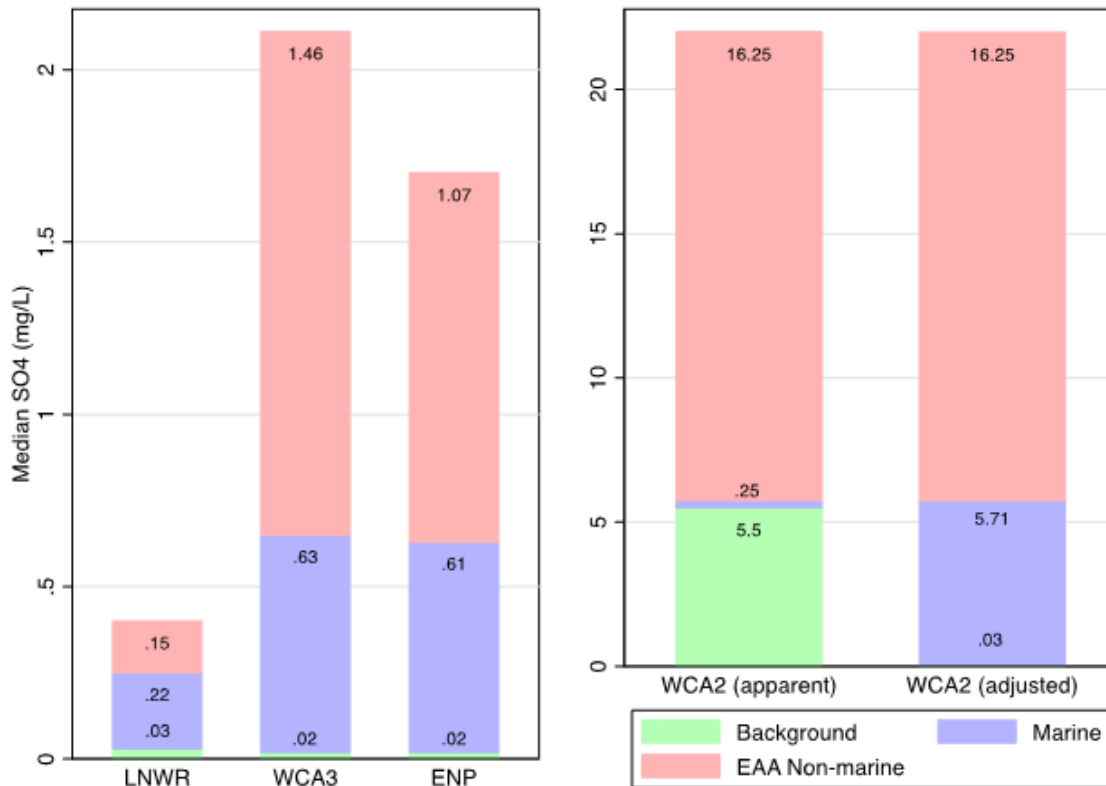


Figure 3B-22. Contributions from different source categories to median SO_4^{2-} concentrations in the Refuge, WCA-2, WCA-3, and ENP. Stack bar length shows the median concentration and is the summed contribution from each individual source. Source contribution categories include excess (non-marine) SO_4^{2-} exported from the EAA (red bar); background contributions (defined as the lower 2.5 percent concentration observed in a given hydrologic unit; green bar); and marine sources, which would be primarily connate seawater (blue bar). WCA-2 is shown separately because of the tenfold scale difference. The analysis for WCA-2 includes both estimates for the apparent background SO_4^{2-} concentration as defined above, and an “adjusted” background concentration defined by the maximum background concentration (0.031 mg/L) (defined as the lower 2.5 percent concentration) inferred for the other three hydrologic units.

SULFUR AND MERCURY GEOCHEMISTRY IN NORTHWESTERN WATER CONSERVATION AREA 2A

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and George R. Aiken¹⁵

As a key water quality issue for Everglades restoration and originating in Lake Okeechobee and the EAA from multiple sources (Bates et al., 2002; Orem, et al., 2011), sulfate enters the EPA in discharges from canals or the Everglades STAs. Sulfate concentrations in Everglades marshes near discharges may average 60–70 mg/L, compared to background levels of less than 1 mg/L in the ecosystem (Scheidt and Kalla, 2007; Orem et al., 2011) and as low as 0.02–0.03 mg/L (Pollman, 2012b). High sulfate loading stimulates microbial sulfate reduction, causing buildup of sulfide in Everglades anoxic soils. Sulfate loading to the ecosystem has also been implicated as a major control on the production and bioaccumulation of toxic MeHg (Orem et al., 2011).

The STAs, designed to remove total phosphorus from surface water through biological uptake, appear to have little effect in reducing sulfate loading to the EPA. Although plants require sulfate in about the same amounts as phosphate, sulfate concentrations in surface waters exceed those for phosphate by more than a factor of 1,000. Therefore, aquatic plants and algae in the STAs that do an efficient job of phosphate removal are unable to significantly reduce sulfate loading from the EAA to the EPA (Pietro et al., 2009).

Northwestern (NW) WCA-2A has experienced a dramatic increase in sulfate levels since STA-2 operations began in July 2001 (Garrett and Ivanoff, 2008), though flow from STA-2 has improved WCA-2A hydroperiod water depth, and reduced frequency of dryout. Prior to that time, this area was rainfall-dominated with SO_4^{2-} concentrations ranging from 5–17 mg/L. The U.S. Geological Survey (USGS) observed sulfate levels of 60 mg/L at sites closest to STA-2 discharges in August 2009 and February 2010, and sulfide levels in porewater ranged from 40– 6,000 $\mu\text{g/L}$. In surface water, measurable sulfide was present at most sites, with levels up to 300 $\mu\text{g/L}$. Most sites had surface water sulfide levels that exceed the USEPA National Recommended Criterion of 2 $\mu\text{g/L}$ undissociated H_2S for protection of fish and other aquatic life (USEPA, 2012b).

Sulfide concentrations in surface water and porewater were correlated with surface water sulfate concentrations. SO_4^{2-} levels in surface water decreased from sites nearest the STA-2 discharge into NW WCA-2A to sites 4 km distant from the discharge at an average rate of 1.64 $\text{mg L}^{-1} \text{ km}^{-1}$. Sulfate declines across the marsh due to removal by microbial sulfate reduction and dilution. The USGS has observed similar rates of SO_4^{2-} loss elsewhere in the Everglades.

THg in surface water ranged from 0.8–4.3 ng/L in August 2009 and from 0.9–2.2 ng/L in February 2010. MeHg concentrations in surface water ranged from 0.04–1.1 ng/L in August 2009 (average 0.44 ng/L) and from 0.04–0.5 ng/L in February 2010 (average 0.19 ng/L). The decline in MeHg concentrations from August to February is hypothesized to be due to a temperature effect on microbial sulfate reduction and mercury methylation rates. THg and MeHg concentrations in surface waters were highly correlated, and MeHg ranged from 3.9 to 28.3 percent of the total mercury in all surface water samples.

MeHg concentrations in NW WCA-2A are elevated relative to areas of the ecosystem far from canal and STA-2 discharges. This may represent stimulation of MeHg production by sulfate entering from STA-2. However, the relationship between SO_4^{2-} loading and MeHg production is complex, as discussed in detail in Orem et al. (2011). While SO_4^{2-} loading stimulates microbial

sulfate reduction and MeHg production, buildup of sulfide (an end product of microbial sulfate reduction) reduce the rate of mercury methylation. In most ecosystems, this results in a unimodal relationship between SO_4^{2-} and MeHg, with maximum MeHg produced at some intermediate SO_4^{2-} concentration (often referred to as the Goldilocks Zone). This type of relationship between SO_4^{2-} and MeHg may exist in NW WCA-2A (**Figure 3B-23**), and the plot of SO_4^{2-} versus MeHg has the characteristic bell shape. USGS studies have suggested similar relationships in the ecosystem at other locations along the SO_4^{2-} loading gradient (Orem et al., 2011). In NW WCA-2A, maximum MeHg concentrations occur at SO_4^{2-} concentrations in the range of 40-60 mg/L, which is much higher than observed in other areas. It is hypothesized that this may be due to the high SO_4^{2-} loading and the fact that such loading in this case is relatively recent. Sulfide concentrations may not have yet reached levels to effectively inhibit MeHg production except at the highest levels of loading. It is also hypothesized that organic peats and possibly metals may still be effectively reacting with sulfide produced by microbial sulfate reduction, sequestering the sulfide as metal sulfides or organic sulfur and moderating the amount of free sulfide present. Over time, as sulfide reactive sites on the organic matter and free metals present are reduced by reaction with sulfide, the sulfate level producing maximum MeHg production is expected to decline. The USGS plans continued monitoring of SO_4^{2-} loading and MeHg production at this site to further understand these relationships.

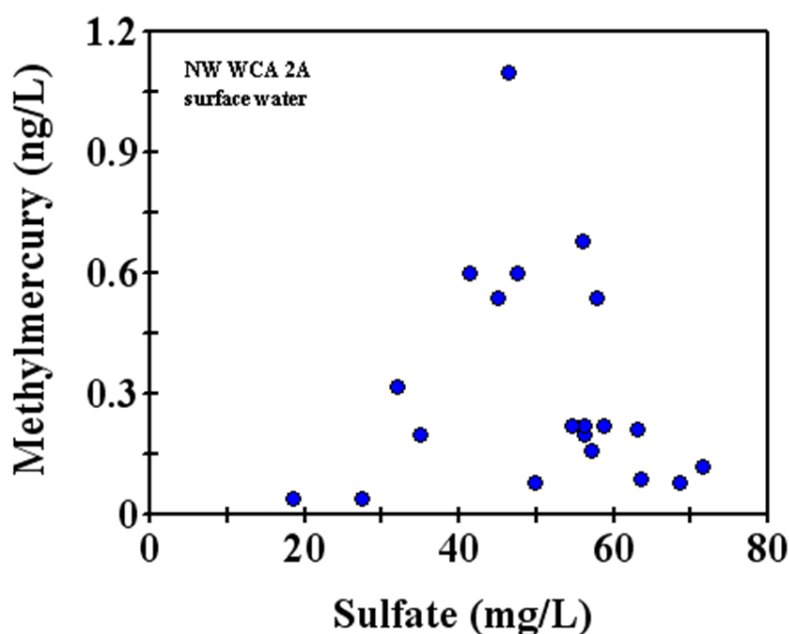


Figure 3B-23. SO_4^{2-} concentration plotted against MeHg concentrations for surface waters of northwest WCA-2A.

DISSOLVED ORGANIC MATTER CONCENTRATION AND CHARACTER IMPACT MERCURY AVAILABILITY FOR METHYLATION

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Dissolved organic matter (DOM) in the Everglades, originating from degradation of peat and leaching and degradation of algae, periphyton, and macrophyte detritus, varies in concentration and character both spatially (Qualls and Richardson, 2003; Scheidt and Kalla, 2007; Wang et al., 2002) and with hydroperiod (Lu et al., 2003; Scheidt and Kalla, 2007). Chemical characteristics of DOM are influenced by source materials (Qualls and Richardson, 2003) and biogeochemical processes, such as microbial metabolism and photo-oxidation (Aiken et al., 2011a).

Everglades marshes naturally support high rates of organic carbon production via photosynthesis; additionally, the flow of agricultural drainage waters from the EAA to the EPA has resulted in nutrient enrichment of historically oligotrophic wetlands in the WCAs. This nutrient enrichment, including phosphorus addition to the northern EPA, strongly influences the nature of DOM by increasing plant production and altering plant community composition (Davis, 1991), increasing the rate of peat accretion (Craft and Richardson, 1993), causing anaerobic conditions in pore waters in the nutrient-rich areas, and increasing the microbial mineralization rate of organic matter (Amador and Jones, 1995) with the subsequent generation of greater concentrations of DOM (Aiken et al., 2011a).

In general, Everglades DOM concentrations are highest in areas influenced by agricultural drainage waters, lower in more pristine locations, and decrease with distance from northern, eutrophic sites in WCA-2A into WCA-2B, WCA-3A, and further south into the Park (Aiken et al., 2011a) (see **Figures 3B-24** and **3B-25**). The character of DOM also changes across the nutrient enrichment gradient of the EPA. For instance, SUVA₂₅₄ (specific UV absorbance per meter at wavelength 254 nm divided by DOC concentration) is a strong indicator of the presence of aromatic compounds and is often related to DOM reactivity (Weishaar et al., 2003). Data presented in **Figure 3B-25** show that SUVA₂₅₄ decreases from north to south, with impacted sites in the northern EPA consistently having the highest values. At sites such as F1 in the northern EPA, SUVA₂₅₄ data are more consistent over time than the DOC concentration data, indicating that even though the DOM concentrations at these locations are temporally variable, the nature or quality of the organic matter is relatively invariant.

The understanding of the role of DOM in Hg methylation is evolving. Hg methylation occurs mainly in mildly sulfidic sediments and soils. New research indicates that nanoparticulate β -HgS(s) (metacinnabar) may be an important, and even the dominant, inorganic mercury species under these conditions (Aiken et al., 2011b; Deonarine and Hsu-Kim, 2009; Gerbig et al., 2011). DOM strongly interacts with β -HgS(s), inhibiting its growth, aggregation, and ordering (Deonarine and Hsu-Kim, 2009; Gerbig et al., 2011; Slowey, 2010). This interaction between DOM and HgS has important implications for Hg bioavailability and MeHg production, as nanocolloidal HgS stabilized by DOM has been demonstrated to be highly bioavailable to Hg-methylating SRB (Graham et al., 2012; Zhang et al., 2012).

Both the concentration of DOM and its chemical character impact the bioavailability of Hg for methylation. DOM character varies in space and time (Aiken et al., 2011a), and the nature of DOM may be expected to influence the strength of interactions with HgS and therefore be an important control on Hg bioavailability and methylation (Mitchell and Gilmour, 2008; Aiken et al., 2011a,b). To test this hypothesis, Hg methylation in Hg-DOM-S solutions was evaluated with

a wide variety of DOM isolates, including DOM from sites 2BS in WCA-2B and F1 in WCA-2A) in the EPA (Gerbig et al., 2011).

Study tests on the role of DOM character on Hg bioavailability for methylation were done under controlled conditions in pure culture of Hg-methylating SRB, *Desulfovibrio desulfuricans* ND132 (Gilmour et al., 2011; Graham et al., 2012). Results showed that DOM character was an important control on Hg methylation in Hg-DOM-S solutions. DOM with a high degree of aromaticity (reflected in high $SUVA_{254}$ values) appears to be especially effective at enhancing Hg methylation, consistent with reports that highly aromatic DOM interacts most strongly with HgS and other metal sulfides (Deonarine et al., 2011; Deonarine and Hsu-Kim, 2009; Waples et al., 2005). Therefore, measures of DOM concentration and quality, in addition to sulfate/sulfide, should be considered in models predicting the sensitivity of ecosystems, including the Everglades, to Hg loads.

Together, these data suggest that DOM in the northern, nutrient-impacted EPA is better able to enhance Hg bioavailability for methylation than DOM in the more pristine marshes. Regional hydrologic restoration is expected to result in changes in the distribution of DOM across the EPA, potentially moving highly aromatic, highly reactive DOM farther south into the ecosystem and, in turn, impacting the production and distribution of MeHg across this area.

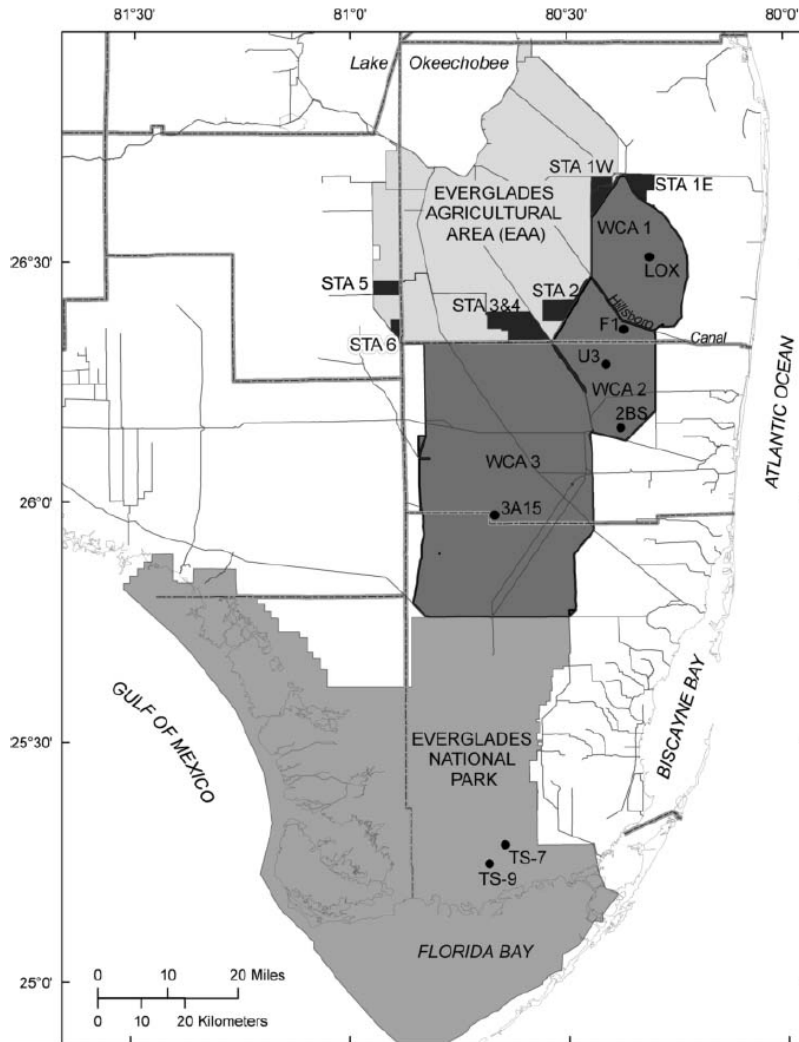


Figure 3B-24. Dissolved organic matter sampling locations in the EPA.

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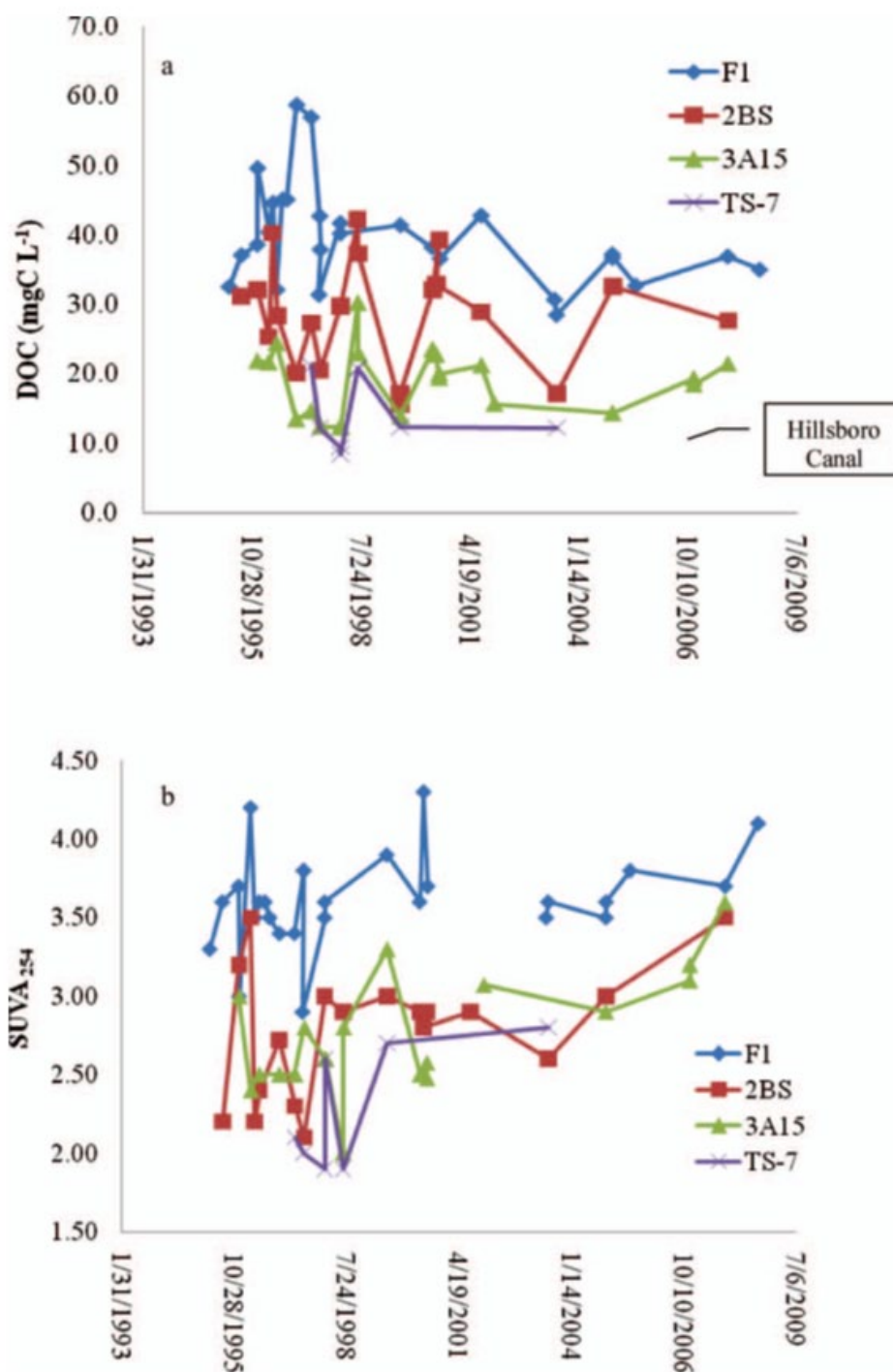


Figure 3B-25. Seasonal and spatial variability in dissolved organic carbon concentration (top) and specific ultraviolet absorbance (SUVA₂₅₄) (bottom) from select sites in the EPA.

SULFUR SOURCES AND EFFECTS

RELATIONSHIPS BETWEEN EMERGENT MACROPHYTE LEAF ELONGATION RATES AND POREWATER SULFIDE LEVELS IN STA-2 CELL 1

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Li et al. (2009) have suggested that southern cattail (*Typha domingensis*) has greater tolerance to sulfide toxicity than sawgrass (*Cladium jamaicense*) and could facilitate *Typha*'s displacement of *Cladium* stands in the northern EPA where elevated levels of phosphorus and sulfur co-occur. In that study, species-specific differences in physiology and growth responses of immature, single stem *Cladium* and *Typha* plants exposed to various sulfide concentrations in hydroponic culture were evaluated. Compared with controls (0 mM sulfide), the net photosynthesis rate for *Typha* was adversely impacted at a porewater sulfide concentration of 0.92 mM (29.5 mg/L), but only half of that sulfide concentration significantly affected *Cladium*.

Differences between *Typha* and *Cladium* among treatments were also found in final rhizome biomass and total live biomass. Both parameters were reduced at 0.69 mM (22.1 mg/L) sulfide for *Cladium*, while they were unaffected for *Typha*. No effects of sulfide on total leaf and root biomass, shoot base biomass, total plant biomass, ratio of live and dead root-supported biomass (leaves, shoot base and rhizomes) to live and dead root biomass (total RSB/RB ratio), as well as on live RSB/RB ratio [(live leaf, shoot base and rhizome biomass)/live root biomass ratio] were detected for either species. *Cladium* leaf elongation (LE) declined from ~0.7 cm d⁻¹ to 0.4 cm d⁻¹ at 7 mg/L sulfide, whereas *Typha* LE was not significantly affected until sulfide concentrations reached 22.1 mg/L, where LE declined from 2.4 cm d⁻¹ to 1.4 cm d⁻¹ (Li et al., 2009).

To further clarify potential adverse sulfide effects in the Everglades, a study was initiated in which field sites characteristic of low and high sulfide levels were periodically monitored for LE of plants in mature stands of *Cladium* and *Typha*. Findings for one of the field study sites (outflow region of STA-2 Cell 1) are briefly discussed here. Since 2000, inflow sulfate levels to STA-2 have been the highest among all the Everglades STAs and WCAs, so this treatment wetland likely represents the most "sulfate-enriched" wetland parcel in South Florida.

Results of the monitoring studies reflected similar LE rates within each species for both 2011 and 2012 (**Figure 3B-26**). The mean LE rates for *Cladium* were 0.54 cm d⁻¹ and 0.63 cm d⁻¹ during the 2011 and 2012 monitoring periods, respectively. In comparison, mean *Typha* LE rates for 2011 and 2012 were 1.76 and 2.16 cm d⁻¹, respectively. Throughout the combined study period, the *Typha* LE rate (2.01 cm d⁻¹) was consistently higher than the corresponding rate for *Cladium* (0.59 cm d⁻¹). Median ratios of *Typha* LE to *Cladium* LE for the 2011 and 2012 monitoring periods were 2.65 and 3.97, with interquartile ranges of 3.26 and 2.95, respectively. These values are substantially lower than the reported LE ratio of 7.1 that was evidence of sulfide toxicity in the laboratory (Li et al., 2009).

Additionally, linear regression analysis of *Cladium* LE versus sulfide concentration demonstrates the lack of significant relationship ($p > 0.05$ for the slope of the regression line) between the two variables (**Figure 3B-27**). Also, no significant correlation was observed between the leaf elongation ratio and porewater sulfide concentration. It should be noted that porewater

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sulfide levels measured in our field study were frequently much higher than the 7 mg/L threshold concentration for *Cladium* growth inhibition observed in laboratory studies (Li et al., 2009).

While *Typha* has been shown to have a greater capacity than *Cladium* for oxidation of the rhizosphere via radial oxygen loss (ROL) from roots (Chabbi et al., 2000), ROL in *Cladium* is moderately high, reaching 75 percent of ROL rates for *Typha*, for plants grown under long-term (two months) flooded conditions. Development of an oxidized rhizosphere can serve as a buffer against inhibitory effects of reduced compounds such as sulfide (McKee et al., 1988; Chabbi et al., 2000). Indeed, porewater monitoring data of this study indicate that sulfide levels tend to decline in close proximity to the plant stems (**Figure 3B-28**), suggesting that an oxidized rhizosphere near the *Cladium* roots may be inhibiting sulfate reduction or oxidizing sulfide.

It should be noted that these data do not necessarily demonstrate a greater tolerance of *Cladium* to sulfide than observed in laboratory conditions, but rather suggest that the relatively low diffusion rate of sulfide in organic soils, calculated to be 16 percent of that in water, results in dramatically lower delivery rates of sulfide to the oxidized root microenvironment than would be achieved under hydroponic conditions, with the aqueous sulfide levels replenished daily (Li et al., 2009). Regardless of the mechanisms responsible, field-based observations indicate that growth of mature *Cladium* plants as determined by leaf elongation rate is not inhibited (relative to *Typha*) by sulfide in one of the most sulfate-enriched Everglades marshes.

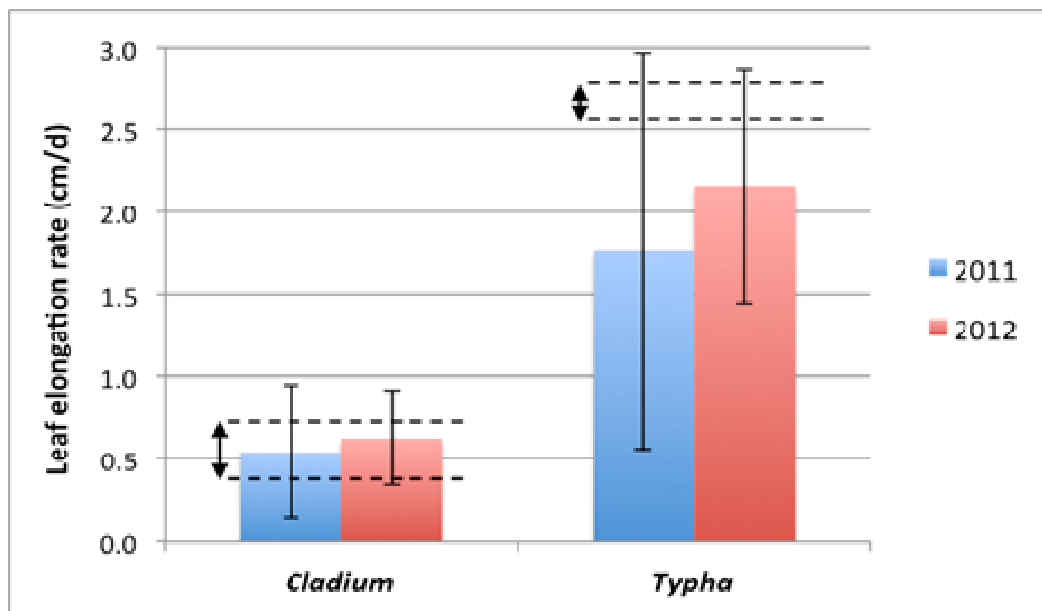


Figure 3B-26. Mean (\pm SD) leaf elongation (LE) rate for *Cladium* and *Typha* plants at the STA-2 Cell 1 study site during 2011 and 2012 monitoring periods. LE was measured for six leaves on each of six plants of each species during seven 2-week growth intervals in 2011 and 13 weekly intervals in 2012. The upper and lower dashed lines represents the LE rates observed by Li et al. (2009) in the laboratory with 0 mg/L and 7 mg/L sulfide, respectively, in the hydroponic solution.

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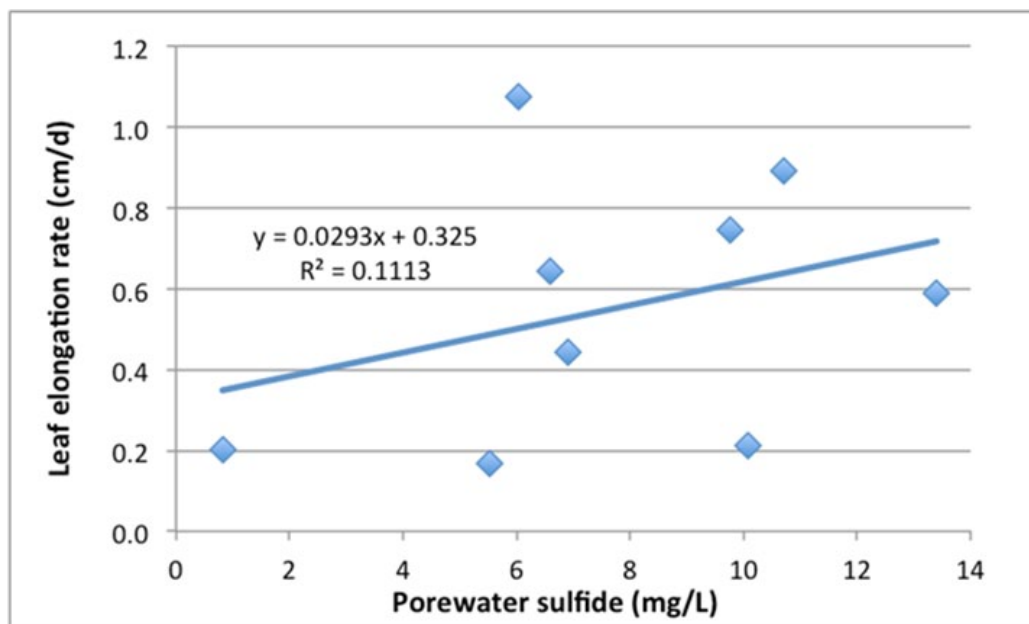


Figure 3B-27. Relationship between *Cladium* LE rate and porewater sulfide concentration, measured at sites located 10 cm from the shoot base of the respective plants. Simultaneous LE measurement and porewater sampling was conducted during the last two events of the 2011 monitoring period and during every other (7 out of 14) 2012 monitoring events.

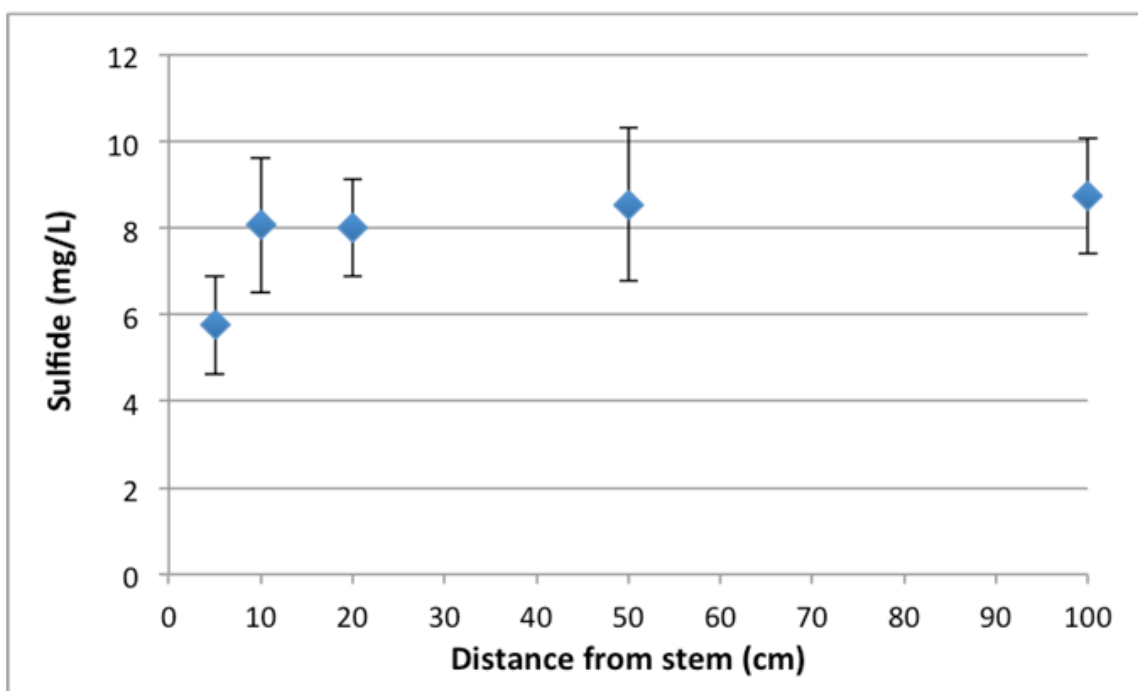


Figure 3B-28. Concentration of sulfide in soil porewater (6-10 cm depth interval) at distances of 5, 10, 20, 50, and 100 cm from the shoot base of triplicate *Cladium* plants within the STA-2 Cell 1 LE monitoring site. Data points represent means \pm SE of concentrations measured at each distance during seven sampling events in 2011 and 2012. Therefore, each data point represents the mean of 21 separate porewater sulfide measurements at a 6–10 cm depth in the soil.

SOIL PH, NUTRIENTS AND SULFUR USE IN EVERGLADES AGRICULTURAL AREA

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Current University of Florida Institute of Food and Agricultural Services (UF/IFAS) fertilizer recommendations suggest application of 500 lb elemental sulfur(S)/acre (agricultural sulfur normally contains 90 percent elemental S) once every 3 years—as sugarcane is typically planted only once every 3 years—for sugarcane production on organic soils with a pH 6.6 or higher. Because of environmental concerns regarding the impact of sulfate on conversion of mercury compounds to harmful MeHg in the Everglades, providing updated fertilizer recommendations to growers that will be cost-effective and minimize sulfur applications is a priority. Assessment of the fate of applied S fertilizers is important in understanding the contribution of the EAA to S cycling in the Everglades. Field demonstrations at multiple sites in the EAA are established to gauge the effectiveness of elemental S applications.

In this study, field work continues to examine sugarcane response to elemental S on high pH organic soils. For the six study locations, yield responses have ranged from no response to a 33 percent increase in tons sugar/acre at the rate of 400 lb S/acre. Results indicate that sugar yield is reduced at $\text{pH} \geq 7.5$ as micronutrient availability is decreased. Leaf manganese concentration has generally been a good indicator of potential yield response to sulfur application, with yield reduced with leaf manganese < 16 mg/kg. An increase in calcium carbonate in the soil results in increased soil pH, and preliminary results indicate that extractable soil calcium may be useful as part of a soil test for predicting sugarcane yield response to sulfur application.

Various S-containing materials, such as elemental S, iron sulfate, and aluminum sulfate, were evaluated for leafy greens production to reduce soil pH and increase nutrient availability. All compounds tested performed similarly and tended to produce similar yield responses. Plant-available nutrient concentrations and soil pH were measured several times in the growing season, and amendments enhanced concentrations of plant-available phosphorus. All amendments were effective at increasing leafy greens yield, with the maximum yield occurring at 500 kilograms/hectare (kg/ha). Rates above 500 kg/ha produced no yield increase. Banded application of amendments was better than broadcast at low rates, but broadcast was better at the higher application rates. At rates below 250 kg/ha, banded application increased yields by 15 percent relative to broadcast application. However, at rates above 250 kg/ha, broadcast application resulted in higher yields than banded. Banded application at high rates had harmful effects on leafy greens growth, as some root burn limited growth resulting in lower yields compared to broadcasting.

In general, soil pH adjustment by S addition has proven temporarily effective, but the large amount and cost required may limit its commercial utilization. For short-duration crops, such as leafy greens, positive benefits in terms of increased nutrient availability and yield have occurred. In contrast, for crops such as sugarcane, which typically remain in the field for 12 months, there was minimal benefit except when soil pH was above 7.5 and the soil contained high calcium carbonate concentrations. The expanded use of fertilizer banding, split application, and foliar application may be viable options to combat the increasing pH.

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FUTURE RESEARCH NEEDS

As presented in the *Future Research Needs* section of the 2012 South Florida Environmental Report (SFER) – Volume I, Chapter 3B, several recommendations for future research needs related to mercury and sulfur environmental assessment for the Everglades were formulated during the interagency 2011 Workshop on Mercury and Sulfur in South Florida Wetlands (Landing, 2011; final peer-review report is available on the SFWMD's website at www.sfwmd.gov/library). Since the June 2011 workshop, coordinated efforts among the District, FDEP, and other stakeholders have continued in order to discuss critical data gaps and refine key recommendations associated with these related research needs, as summarized below.

SULFUR MASS BALANCE STUDIES

While there is compelling evidence that sulfate promotes conversion of inorganic mercury to MeHg by SRB in the Everglades and that the EAA is a key source of sulfate to the EPA, very little is still known about regional sulfur cycling on both small and large scales. An accurate sulfur mass balance is critical to better understanding the sulfur cycling in South Florida and for identifying any opportunities to sufficiently reduce SO_4^{2-} loading to the EPA, which could potentially lower MeHg levels in Everglades fish, and decrease risk to recreational anglers and fish-eating wildlife.

The SFWMD's Sulfur Action Plan includes sulfur mass balance as a key research goal (SFWMD, 2011). There are large uncertainties regarding the rate of agricultural application of sulfur in the EAA, rate of sulfur release from oxidation of EAA soils, and source(s) of the high sulfur levels in EAA soils. Additional research on EAA soil sulfur dynamics is needed to estimate soil sulfur content and character and the time required for soils to reach natural sulfur levels in the absence of agricultural application of sulfur. The sulfur mass balance should include analyzing the effects of backpumping sulfate-enriched waters from the EAA on SO_4^{2-} concentrations in Lake Okeechobee, as well the effects of other sources, including internal supply of sulfate resulting from soil oxidation of reduced sulfur and agricultural inputs entering Lake Okeechobee through the Kissimmee River. Further study is also warranted to evaluate recent modeling that hypothesized that connate seawater is a significant source of SO_4^{2-} to the EPA, to quantify atmospheric depositional sulfur contributions and the contribution and proximate sources of SO_4^{2-} inputs from Lake Okeechobee to the EAA, and investigate the viability of sulfur removal options in the EAA.

MONITORING AND MODELING

Comprehensive, long-term monitoring in Everglades media has provided a valuable database to help examine trends and enhance understanding of various processes in the regional system. Importantly, there is a continued need to monitor atmospheric mercury deposition, MeHg accumulation in fish and other biota, and water quality, especially SO_4^{2-} concentrations. Currently, these monitoring activities are conducted by the District under the Everglades Forever Act mandates and reported in the annual SFER. Also, the USGS and University of Florida continue to conduct field studies to assess the relationships of DOC, SO_4^{2-} , and MeHg in biota.

It is widely accepted that the ability to reliably predict how any system will respond to changes in inputs or outputs or internal cycling rates requires the use of models. The Everglades Mercury Cycling Model (E-MCM) is a dynamic model that includes various rate equations covering the important mercury cycling processes in the Everglades. Further efforts are necessary to develop this model to be applicable to widely varying conditions found throughout the system, including the EAA, STAs, WCAs, and ENP.

To assess the effects of possible intrusion of connate seawater, it is recommended that a coupled hydrologic and water chemistry model be developed that includes both chloride and sulfate dynamics and incorporates explicit representations for groundwater interactions with overlying water across the Everglades landscape. It is desirable that such a model also be capable of simulating how the hydrologic alterations imposed by the Comprehensive Everglades Restoration Plan will influence surface water chloride and sulfate concentrations, and enable computations of the effect of changing EAA inputs of agricultural and connate seawater SO_4^{2-} as well as the effect of changes in the sulfate anthropogenic component of atmospheric deposition.

Additionally, the Everglades Landscape Model (ELM) may be adapted to include sulfur cycling. It is important for some of these models to include a detailed account of the current movement of water throughout the system as well as associated environmental variables (e.g., dissolved oxygen, DOC, and pH) monitored by the District.

The District has conducted preliminary data analysis on a sulfate budget for Lake Okeechobee. The Lake Okeechobee Environmental Model (LOEM) has a module capable of simulating lake-wide changes in SO_4^{2-} concentrations under various hydrological conditions. There is also interest in conducting data analyses using historical water quality data (SO_4^{2-} , DOC, color, etc.) from the SFWMD's monitoring network to document historical trends of sulfate concentrations and the relationships among sulfate, DOC, and THg in fish. Such analyses are also expected to be useful for modeling efforts in a hind-casting perspective.

DISSOLVED ORGANIC MATTER

Dissolved organic matter has been shown to influence the bioavailability of Hg to SRB, influence the binding of Hg^{2+} to sediments, and be involved in the photochemical reduction of Hg^{2+} and the photochemical breakdown of MeHg. Dissolved organic carbon, a substitute for DOM, is included in the District's water quality monitoring network for selected sites. Historical data for DOC are also available in the District's DBHYDRO database (www.sfwmd.gov/dbhydro). While the role of DOC on mercury methylation in the Everglades has been initially evaluated, more research is needed to better understand the importance of the composition and level of DOM on MeHg production. Also, because higher DOM concentrations and greater levels of aromatic DOM—which is most effective in making Hg^{2+} bioavailable for methylation by SRB—are present in the northern, nutrient-impacted EPA, it is key to examine the causes for the elevated DOM to determine possible opportunities to reduce such levels.

EFFECTS OF SULFATE ON MERCURY METHYLATION AND DEMETHYLATION

Available research indicates that the relationship between sulfate concentration and mercury methylation rate is nonlinear and unimodal, and that the maximum methylation potential associated with sulfate varies across the Everglades. Because the magnitude and direction of the effect of sulfate reductions is so sensitive to the shape of relationship and the locus of the sulfate maximum, the effects of changing sulfate on mercury methylation—particularly at low ambient concentrations (i.e., from ~detection limit to 5 mg/L)—would benefit from further evaluation. Because the growth of SRB is stimulated in the presence of both SO_4^{2-} and DOM, the interaction of SO_4^{2-} and DOM loadings on mercury methylation rate also requires more research.

Previous and current studies indicate that demethylating bacteria can significantly reduce MeHg concentrations in the Everglades. However, little is known about the factors that promote demethylation. An understanding of the role of demethylation in the MeHg mass balance may help clarify the variations of MeHg in wildlife in different marsh areas that cannot be explained by sulfate concentration and mercury methylation potential and lead to management alternatives that promote activity of demethylating bacteria.

BIOACCUMULATION OF METHYLMERCURY IN FOOD CHAIN

MeHg concentrations increase up the food chain and display large variations in Everglades fish that cannot be explained by MeHg concentrations in surface water. Limited available data show that the percentage of MeHg in total mercury in fish, especially in low trophic level fish (e.g., *G. holbrooki*), change seasonally in response to diet availability (i.e., detritus versus periphyton). There are also large variations in mercury in high trophic level fish. Initial assessments suggest that these variations might be associated with fish trophic position affected by prey types (i.e., grass shrimp versus sunfish for LMB). Further studies are needed to assess seasonal changes in MeHg concentrations in fish at different trophic levels and the relationships with periphyton MeHg concentration, dietary composition, and MeHg concentrations.

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